

# **Measurement and the Discreteness of Matter**

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Evidence for Discreteness and the Extension of Molecular Motion  
in the Brownian Movement

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## I: Introduction

Jean Perrin was awarded the 1926 Nobel Prize in Physics for his researches that "put a definite end to the long struggle regarding the question of the physical reality of molecules".<sup>1</sup> He had experimentally verified the diffusion, distribution, displacement, and rotational motion of granules in an emulsion in his studies on the Brownian movement. In *Les Atomes*, Perrin enumerated these studies and also explained work by his contemporaries on other phenomena that supported molecular reality.

Establishing the physical reality of molecules minimally amounts to establishing that matter is discrete, but in no way does it amount to imagining the fundamental state of matter as it is – to do that is impossible. As Heisenberg put it, “the atom of modern physics can only be symbolized by a partial differential equation in an abstract multidimensional space” [Heisenberg, p. 38]. At the same time, discreteness was not established in isolation. Perrin’s argument for it rests on the measurement of Avogadro’s number  $[N]$ , the number of atoms or molecules in a mole of a substance. A measurement of  $N$  amounts to a measurement of molecular magnitudes.<sup>2</sup> Atoms and molecules have certain well-defined properties and Avogadro’s number is the connecting link to these properties.

It is instructive to look at Perrin’s argument for discreteness because the general opinion overwhelmingly swung in favor of molecular reality after his experimental work on the Brownian movement in 1908. Concessions of molecular reality started from this point onward and continued up till the 1913 publication of *Les Atomes*, where Perrin

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<sup>1</sup> Carl Wilhelm Oseen in his presentation speech to Perrin’s 1926 Nobel Prize in Physics.

<sup>2</sup> To what extent this measurement is measuring discrete atoms or molecules is another thing and is the whole point in question.

explained several different methods to find  $N$ .<sup>3</sup> It is informative to look at measurement because indirect or direct access to molecular magnitudes is within the measurement procedure. Ostwald had this to say on the relationship between measurement and access:

If a thing exists which possesses a definite numerical value that can be expressed in producible units and which can not be changed by any known process it will fulfil in the highest degree all the requirements that can be made of a reality [Ostwald, p. 496].

Ostwald then said that the mechanistic hypothesis, which assumes atoms and molecules, had “no reference to observable magnitudes” [Ostwald, p. 497]. He made these comments in 1907. Perrin published his experimental work in 1908.

An obvious question surrounds this episode: *did Perrin really put a proper end to the long struggle regarding the physical reality of molecules?* It is conventional wisdom that Perrin settled this question in favor of molecular reality, which no one could do before him.<sup>4</sup> Before looking at the evidence for how Perrin settled this question, here is a brief look at the evidence for discreteness before Perrin.

## **The Case for Discreteness before Perrin**

### *Discrete particles: the link underlying various phenomena*

Maurice Mandelbaum formulated the problem of empirically settling the question of discreteness as the problem of “transdiction”.<sup>5</sup> How do we justify our beliefs

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<sup>3</sup> See Mary Jo Nye’s *Molecular Reality* for concessions of discreteness by different scientists in 1908 including Stephen Jahn [p. 149], Walter Nernst, Svante Arrhenius, Wilhelm Ostwald [p. 150-52], and Henri Poincaré [p. 157]. More concessions followed the publication of *Les Atomes* and there were positive responses by people including Lucien Poincaré [p. 161], William Ramsay [p. 162], J.J. Thomson [p. 163], and Pierre Delbet [p. 164] among others.

<sup>4</sup> Bas van Fraassen disagrees with the conventional wisdom and, instead, calls it **LORE**. In a 2009 article (*The perils of Perrin, in the hands of philosophers*), he suggests that the concessions of molecular reality following Perrin’s work were a bandwagon effect instead [van Fraassen, p. 22; footnote 20].

<sup>5</sup> Mandelbaum borrows the term “transdiction” from Donald C. Williams, who used it in response to a paper delivered by Carl G. Hempel before the Harvard Philosophy Club in 1958. Hempel had

concerning the ultimate constituents of the physical world, without contradicting the important role of experience in human knowledge? Robert Boyle was one of the first experimental scientists to have argued for the discreteness of matter. He thought of it as more than just “the most simple and fruitful hypothesis” [Mandelbaum, p. 89]. Boyle defined how the discreteness claim differed from other conceptions and, in work after work, proved the advantages that it had over alternatives. These works included his *History of Fluidity and Firmness, Experiments and Considerations Touching Colours, New Experiments and Observations touching Cold*, and his *Experiments and Notes about the Mechanical Origin and Production of divers particular Qualities* where he took up the mechanical explanation of heat and cold, tastes, odors, volatility and fixedness, electricity, magnetism, and other phenomena [Mandelbaum, p. 96].

Boyle gave an account of the above phenomena by what he called the “corpuscular philosophy” and did not call it a discreteness claim. The central tenet, either way, is that matter is discrete. Pierre Gassendi initiated the corpuscular philosophy before Boyle and derived his conception from Lucretius. The corpuscular philosophy also influenced Isaac Newton and Walter Charleton. Newton, Charleton, and Boyle formed the backbone of the corpuscular tradition in seventeenth century England.

Boyle admitted that there was a conjectural element to the corpuscular philosophy, but at the same time he noted that it was an intelligible cause of phenomena. He said:

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been speaking of the conditions under which we can predict or retrodict from data given at a certain time to what will happen or what has happened at another time. In Hempel’s discussion, both the observed data and the predicted or retrodicted events were assumed to be directly experienceable. Williams wished to use data to not only move back and forth within experience, but to be able to say something meaningful and true about what *lay beyond* the boundaries of direct experience – this he termed “transdiction” [Mandelbaum, p. 61].

The more numerous, and the more various the particles [i.e. “particulars”] are, whereof some are explicable by the assigned hypothesis, and some are agreeable to it, or, at least, are not dissonant from it, the more valuable is the hypothesis, and the more likely to be true. For it is much more difficult, to find an hypothesis, that is not true, which will suit with many phaenomena [sic.], especially, if they be of various kinds, than but with few”.<sup>6</sup>

This is similar to what Duhem says in *Aim and Structure*:

If the theory is a purely artificial system, if we see in the hypotheses on which it rests statements skillfully worked out so that they represent the experimental laws already known, but if the theory fails to hint at any reflection of the real relations among the invisible realities, we shall think that such a theory will fail to confirm a new law... If, on the contrary, we recognize in the theory a natural classification, if we feel that its principles express profound and real relations among things, we shall not be surprised to see its consequences anticipating experience and stimulating the discovery of new laws; we shall bet fearlessly in its favor [Duhem, p. 28].

That said, confirmation of numerous and various phenomena on the corpuscular theory did not establish the discreteness of matter according to Duhem. The discreteness of matter may explain various phenomena, but that does not make it their cause.

The way Boyle went about confirming the corpuscular theory, there was no *experimentum crucis* that would support it. Support had to be cumulative, over a range of phenomena. Boyle gave an account of numerous and various phenomena using the corpuscular theory, but this only showed that the corpuscular theory is not incompatible with the phenomena. Boyle did not produce much in the way of rigorous derivations of the corpuscular theory from phenomena or of phenomena from the corpuscular theory.

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<sup>6</sup> From the Preface to Boyle’s *Experiments, Notes, &c. about the mechanical origin or production of divers particular qualities*, Works, IV, p. 234 [Quoted from Mandelbaum, p. 105].

The link he made between the observed and the unobserved was rather tenuous, to which Ostwald's general objection to the discreteness of matter, more than two centuries after Boyle, would still apply: "[the mechanistic philosophy] has no reference to observable magnitudes". This objection became more relevant with the development of the kinetic theory of gases, but is also applicable to Boyle's argument for the discreteness of matter. Boyle's tenuous link from the observed to the unobserved was also questionable because he linked the two by extension of sense knowledge through analogy. This principle was fundamentally flawed because all sensible objects are further divisible whereas unobservable atoms are denied this property.

### *Accommodating the facts of Chemistry*

Dalton was arguably the first one to come up with a rigorous account of an atomic theory. The question of the discreteness of matter became acute at least starting from 1808 when he published the first part of his *New System of Chemical Philosophy*. Dalton made the key assumption that chemical compounds are made of "ultimate particles" or atoms, and the least part of a chemical compound is made up of a characteristic combination of atoms of one or more component elements.<sup>7</sup> Dalton knew from the work of Lavoisier and Proust that the weight of each component element is preserved in chemical reactions. Their work also established that the proportions in which two elements combine cannot vary continuously, which led to the Law of Definite Proportions or Proust's Law. Proust's contemporary Claude Louis Berthollet opposed this law based on the continuously varying proportions in metal oxide samples. Proust

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<sup>7</sup> See Section 4.1 [**Dalton's Atomism**] of *Atomism from the 17<sup>th</sup> to the 20<sup>th</sup> century* in the Stanford Encyclopedia of Philosophy for an overview of Dalton's work.

overcame this objection by making a distinction between pure chemical compounds and mixtures to reconcile the seemingly anomalous cause of metal oxides [Rocke, p. 7].

Dalton himself confirmed Proust's Law for oxides of nitrogen and hydrocarbons, such as methane and ethylene. Case after case confirmed that the masses of elements in compounds vary discontinuously. Proust's law implied that the masses of two elements entering into various compounds would vary in a simple ratio to each other. This became the Law of Multiple Proportions, which Dalton verified in his studies of the oxides of nitrogen and the hydrocarbons mentioned above.<sup>8</sup> By 1808, Thomas Thomson and W.H. Wollaston independently announced additional examples of multiple proportions, pointing them out as simple consequences of Dalton's chemical atomism [Rocke, p. 35].

Dalton considered success in accommodating chemical phenomena as providing evidence for the physical atom. However, the chemistry of the time could be accommodated without making that concession. Berzelius introduced chemical formulae based on results of gravimetric analyses and the laws of proportions, but this did not necessitate the physical reality of atoms.

In *Chemical Atomism in the Nineteenth Century: From Dalton to Cannizzaro*, Rocke argues that chemists in the early nineteenth century had all bought into the chemical atom, but most remained agnostic on the question of the physical atom. In other words, the question of the physical reality of atoms and the discreteness of matter was still wide open. Dalton's theory gave an explanation of the Laws of Definite and Multiple Proportions, Gay-Lussac's Law of Combining Volumes, Avogadro's Hypothesis, and Dulong and Petit's Relation. These relations could all be reconciled by reference to the

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<sup>8</sup> To be less anachronistic, Dalton referred to methane and ethylene as "olefiant gas" and marsh gas (or "carburetted hydrogen") respectively [Rocke, p. 34].

chemical atom, which did not necessitate the physical reality of the atom. There were rigorous consequences going from the atomic conception to phenomena, but not vice-versa.

### *Causal-eliminative support for atoms*

Dalton's theory also implied that different structural arrangements of discrete atoms could in principle lead to different compounds. This became significant when Gay Lussac and Liebig published their discovery of the chemical composition of silver fulminate (Ag-CNO) and silver cyanate (Ag-OCN) in 1826. This was followed by Wöhler's transformation of ammonium cyanate into isomeric urea (1828) and Berzelius' discovery of the identity of racemic acid and tartaric acid (1830) [Nye, p. 4]. The concept of isomerism – compounds of identical chemical composition with different structural arrangements – explained the chemical similarities of these compounds and became one of the strongest arguments for the atomic conception. There was no way to explain isomerism except on the assumption of physically real and distinct atoms.

Nevertheless, the dispute regarding the physical reality of atoms continued. Just because there was no alternative explanation at the time did not preclude alternative explanations developing in the future. Kekulé made the following remark on the ultimate structure of matter:

The question whether atoms exist or not has but little significance from a chemical point of view; its discussion belongs rather to metaphysics... From a philosophical point of view, I do not believe in the actual existence of atoms... I rather expect that we shall some day find for what we now call atoms a mathematico-mechanical explanation which



will render an account of atomic weight, of atomicity, and of numerous other properties of the so called atoms.<sup>9</sup>

It was not incredible for Kekulé to say this since Maxwell's system of equations had been developed around the same time. Everyone agreed with Maxwell's system of equations, even though there were numerous mutually exclusive physical models that could represent Maxwell's theory of electromagnetism. Maxwell's theory was for the dynamics of a continuum – the electromagnetic field – and reconciling continuum physics with discrete theories was another problem widely recognized in nineteenth century England.

### *Quantitative derivations from the kinetic theory of gases*

The development of the kinetic theory of gases became another facet to establish the discreteness of matter. Maxwell mathematically refined Clausius' work on the kinetic theory in 1859, which was further developed by Boltzmann. The kinetic theory explained the gas laws connecting volume, pressure, and temperature. It explained Avogadro's Law, thereby also explaining Gay-Lussac's law. It led to novel predictions, some of which were counter-intuitive, for instance that the viscosity of a gas is independent of its density, which was confirmed experimentally. The kinetic theory also revealed the relation between gaseous and osmotic pressure, which, according to Poincaré, would have remained profoundly hidden without it [Poincaré 1905, p. 162-163].

This success was still undermined by the problem that rigorous derivations were going from the assumption of the discreteness of matter to observed phenomena, but not vice-versa. The correlation between the kinetic theory and empirical laws did not by itself comprise sufficient access to unobservable atoms and molecules, and the novel relations revealed by the kinetic theory of gases could in principle be revealed by other underlying

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<sup>9</sup> Quoted from pp. 4-5 of Nye's *Molecular Reality*.

mechanisms. The latter possibility can be seen in the cautionary example of Newton's derivations in optics, where he was able to accurately derive several empirical laws from contradicting wave and particulate conceptions of light.

### *Accessing molecular magnitudes*

It seems that arguments for the discreteness of matter before Perrin failed to properly access molecular magnitudes. Ostwald criticized the discreteness of matter on exactly this point when he said that the mechanistic hypothesis had no reference to observable magnitudes. To fulfill this latter requirement was devoted the effort to determine Loschmidt's or Avogadro's number.<sup>10</sup> It was the measurement on which Perrin's argument for the discreteness of matter ultimately rested. Attempts at its determination had been made before Perrin. In 1870, Lord Kelvin published four independent determinations of Loschmidt's number. Finding comparable values, he concluded:

The four lines of argument which I have now indicated lead all to substantially the same estimate of the dimensions of molecular structure. Jointly they establish with what we cannot but regard as a very high probability the conclusion that, in any ordinary liquid, transparent solid, or seemingly opaque solid, the mean distance between the centres of contiguous molecules is less than the hundred-millionth, and greater than the two thousand-millionth of a centimeter [Kelvin, p. 296].

In this quote, Lord Kelvin implicitly acknowledges that convergence of  $N$  was relevant to establishing the discreteness of matter. By 1913, Perrin and his contemporaries had measured convergent values of  $N$  by thirteen different methods.

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<sup>10</sup> Both Loschmidt's and Avogadro's number are the number of molecules in a standard reference. The standard is a cubic centimeter of a gas at STP for Loschmidt's number and a mole of a substance for Avogadro's number. For our purposes, the important point is that they both represent the number of molecules in some standard reference.

The convergent measurement of Avogadro's number by means of distinct indirect measures became the salient feature in the argument for molecular reality. Different measurements, involving different ties to Avogadro's number of measurable parameters, yielded more or less the same value of  $N$ . The more the variously determined values of  $N$  were the same, the greater was the convergence. Lord Kelvin found sufficient convergence in his estimates of Loschmidt's number to conclude with "a very high probability" not only that molecules exist, but also that we know their distance apart at standard conditions. Perrin concluded *Les Atomes* by a similar argument for molecular reality – based on the convergence of  $N$  derived from widely different phenomena, he concluded, "the real existence of the molecule is given a probability bordering on certainty" [Perrin 1913 b, Para. 119].

Lord Kelvin and Jean Perrin stood at opposite ends of the search for Avogadro's number. Both believed that we can prove that molecules exist without actually seeing them, and the principle behind that rests on convergence. The important question then is this: how can the convergence of  $N$  across phenomena establish the discreteness of matter?

## II: The Experimental Work in *Les Atomes*: Thirteen Equations to calculate Avogadro's Number

### **The Point in Question**

Perrin measured Avogadro's number in his famous Brownian movement experiments in 1908, but there had been estimates before him.<sup>11</sup> Loschmidt made the first estimate in 1865 by comparing the molecular volume of air to the net molecular volume in a cubic centimeter at STP. He estimated Loschmidt's number as  $1.9 \cdot 10^{19}$ , which is approximately  $40 \cdot 10^{22}$  for Avogadro's number. As noted above, Lord Kelvin found convergent values of  $N$  by four different methods as early as 1870. Although Kelvin's measurements did not convince scientists at large of the discreteness of matter, he was onto something in suggesting that the discreteness of matter is tied to counting atoms or molecules.

As the investigation into molecular reality unfolded, Perrin's measurements accomplished what Kelvin's or any other measurements before Perrin could not. He convinced scientists at large of the discreteness of matter. Stephen Brush put it best, "The willingness of scientists to believe in the 'reality' of atoms after 1908, in contrast to previous insistence on their 'hypothetical' character, is quite amazing" [Brush, p. 34]. However, it is not obvious why Perrin's results led to the overwhelmingly positive response. This confounded even Brush, who said:

The evidence provided by the Brownian movement experiments of Perrin and others seems rather flimsy, compared to what was already available from other sources. The fact that one could determine Avogadro's number and the charge on the electron by one more

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<sup>11</sup> Stephen Brush has noted estimates of molecular magnitudes by Loschmidt as early as 1865 and similar estimates published by Lothar Meyer, L. Lorenz, G. Johnston Stoney, and Lord Kelvin during 1867-70 [Brush, footnote 32].

method seems hardly sufficient to justify such profound metaphysical conclusions.

[Brush, p. 34].

The point in question then is what exactly was the special significance of Perrin's results that was absent in previous results. The results in Perrin's *Les Atomes* included measurements apart from Perrin's work on the Brownian movement, and he stressed their important role in establishing the discreteness claim. In fact, Perrin devoted most of *Les Atomes* to work he was not directly involved in, and 9 of the 13 featured equations to find  $N$  in that text derive off such work. The discreteness claim seems to rest on convergence not just from Perrin's experimental work on the Brownian movement, but also on other experiments to a greater or lesser extent. In what follows, I will lay out the various measurement procedures that lead to the convergent value of  $N$  in order to analyze what, besides the numerical convergence of  $N$ , suggests the discreteness of matter in the details of the experiments.

## **A Hypothetico-Deductive Approach**

### *Rigorous derivations from the kinetic theory – Equation I*

Convergence of Avogadro's number was sought with values derived from the kinetic theory of gases. The kinetic theory assumed the reality of discrete atoms and molecules<sup>12</sup> and rigorously derived relationships of directly measurable parameters. Molecular agitation explained pressure, and temperature became a measure of the agitation. Qualitative explanations were then rigorously developed into quantitative relationships. Assuming only the independence of orthogonal motions of atoms and

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<sup>12</sup> Henceforth, I'll refer to the discrete particles assumed by the kinetic theory as molecules even though they can be monatomic in specific cases, like the noble gases. Molecules are the discrete, fundamental units of a compound and that's the relevant point for our discussion.

molecules, Maxwell related molecular magnitudes to directly measurable parameters. He found that:

$$\frac{3}{2}PV = \frac{1}{2}MU^2 = W$$

Here  $P$  is pressure,  $V$  is volume,  $M$  is the net molecular mass,  $U^2$  is the square of the mean speed of the molecules, and  $W$  is their mean translational energy.

Clausius, who introduced the idea of mean free path of molecules between collisions, derived a relationship containing Avogadro's number by relating it to the diameter ( $D$ ) of molecules, their mean free path ( $L$ ), and their volume ( $V$ ). Maxwell corrected Clausius' derivation for the motion of molecules relative to one another to give the following:

$$N\pi D^2 = \frac{V}{L\sqrt{2}} \quad [1.1]$$

Mean free path values had been inferred for various gases from viscosity measurements, but a second relationship was needed to find values for the two unknown constants  $N$  and  $D$ . Resolution was found in Van der Waal's equation, which corrected for cohesive forces between atoms and molecules:

$$\left(P + \frac{A}{V^2}\right) \times (V - 4B) = RT \quad [1.2]$$

The parameters  $A$  and  $B$  can be experimentally determined. As of 1913, Perrin's choice value of  $N$  based on the kinetic theory was from experiments on monatomic argon.<sup>13</sup> The value of  $N$  came out as  $62 \cdot 10^{22}$ .

The kinetic theory suggests an incredibly small world of atoms and molecules characterized by incredibly large numbers. Results from the kinetic theory suggested that

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<sup>13</sup> Monatomic argon best approximates a sphere [Perrin 1913 b, Para. 49].

each molecule of the air we breathe is moving with the velocity of a rifle bullet, is deflected from its course 5,000,000,000 times per second, and along with about twenty thousand million other molecules makes up one thousand-millionth of a milligram. Perrin remarked, “The kinetic theory just excites our admiration” [Perrin 1913 b, Para. 49].

While the kinetic theory may have excited the admiration of scientists, it did not remove their skepticism about the discreteness of matter. Perrin thought this skepticism was rightly founded due to the many hypotheses involved in developing the kinetic theory. At the same time, he believed that if entirely independent routes of investigation led to the same values for the molecular magnitudes, faith in the kinetic theory would be “considerably strengthened”. After going over his experimental results on the Brownian movement in *Les Atomes*, Perrin asserts that the “considerable strengthening” essentially amounts to establishing the discreteness of matter.

## **Independent Routes to the Molecular Magnitudes**

### *The Brownian movement*

Perrin’s results on the Brownian movement are salient in making the case for the discreteness of matter. By the time he came on the scene, many aspects of the Brownian movement had already been described. It had been known for a long time that the movement was not peculiar to organic bodies. In his observations from June, July, and August of 1827, Robert Brown, using a lens with a focal length of about  $\frac{1}{32}$  of an inch, found that the Brownian movement persisted in inorganic bodies such as window-glass, several simple earth minerals and metals, rocks of all ages, the minerals of granite, and a

fragment of the sphinx.<sup>14</sup> Experimental work suggested that the movement was persistent. In his observations of 1827, Brown found that dried plant specimens that had been preserved in a herbarium for upwards of twenty years and even a century still maintained evident motion [Brown, p. 471].

By the time Perrin wrote *Les Atomes* he could cite experimental work showing that the Brownian movement continued for days, months, and years inside small closed cells and persisted in liquid inclusions that had remained shut up in quartz for thousands of years [Perrin 1913 b, Para. 50]. The irregularity of the movement had been well documented: adjacent granules remained uncoordinated when temperature, pressure, and light were kept constant. Moreover, the irregular granular motion precluded general current flows as the cause of the movement. The movement was also confirmed independent of granular density or material and was more active the less viscous the fluid. The cause of the movement remained hidden, but when Perrin came on the scene, there was renewed interest in putting the molecular origin of the movement to experimental test.

Before the invention of the ultramicroscope in 1903 by Siedentopf and Zsigmondy, Felix Exner most accurately studied the Brownian movement using an Abbe microscope. He published his results in 1900, concluding that the kinetic theory was not an adequate explanation for the Brownian movement because the kinetic energies of granules based on apparent mean velocities were neither proportional to the absolute

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<sup>14</sup> Brown eased his readers into this by first saying, “In plants, either dried or immersed in spirit for a few days only, the particles of pollen of both kinds were found in motion equally evident with that observed in the living plant”. He moves onto minerals and mentions only a few of the ones he had studied: “travertine, stalactites, lava, obsidian, pumice, volcanic ashes, and meteorites from various localities”. Brown continued, “Of metals I may mention manganese, nickel, plumbago, bismuth, antimony, and arsenic” [Brown, pp. 471-472].



temperature nor comparable to those assumed for molecules in the liquid state.<sup>15</sup> In general, scientists who attempted to measure granular velocities in the Brownian movement obtained a collection of wildly varying results, none of them in agreement with the equipartition theorem of statistical mechanics. This was evident in a table of results of Regnault, Wiener, Ramsay, Exner, and Zsigmondy from 1909 [Brush, p. 23-24]. Jürgen Renn has remarked that the Brownian movement emerged as a veritable challenge to classical physics by the turn of the twentieth century. The kinetic theory had emerged as the most viable option for explaining the phenomenon, yet failed to provide an adequate quantitative understanding [Renn, p. 26].

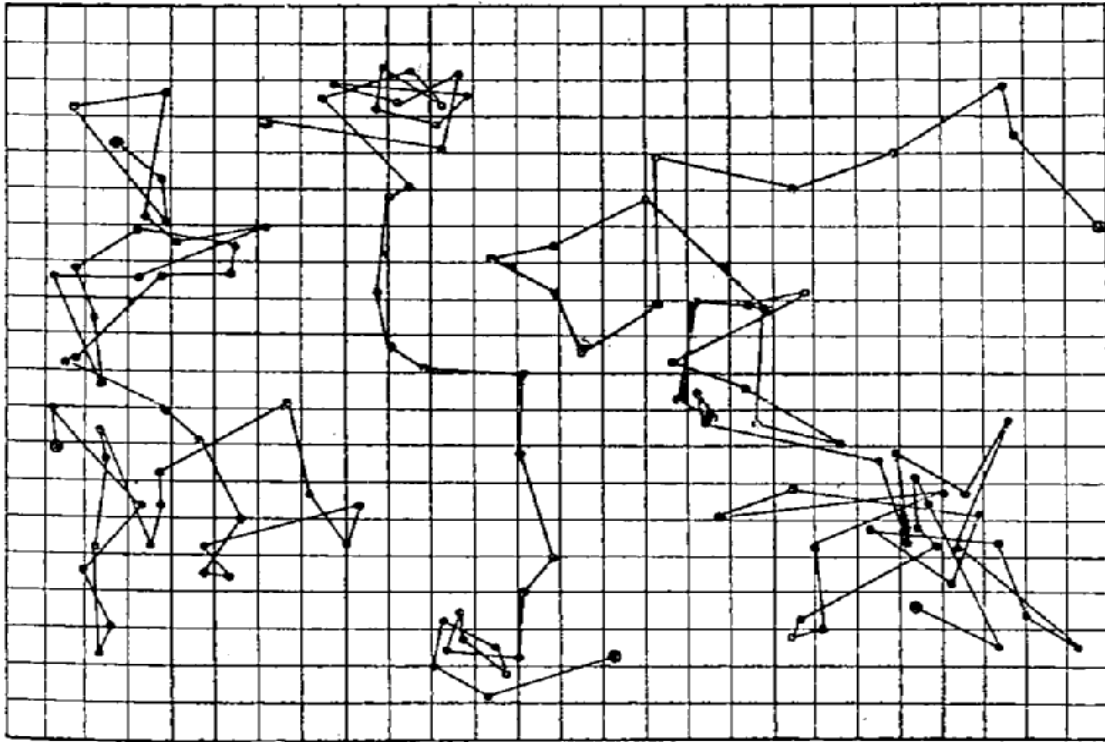
Looking back at discrepant velocity measurements in the Brownian movement, Brush has gone as far as to say, “One can hardly find a better example in the history of science of the complete failure of experiment and observation, unguided (until 1905) by theory, to unearth the simple laws governing a phenomenon” [Brush, p. 23]. The velocity measurements could only become meaningful within a theoretical framework. Discrepant velocity measurements became a source of doubt for the kinetic theory instead, to which Perrin laments in *Les Atomes*:<sup>16</sup>

I have been very much struck by the readiness with which at that time it was assumed that the theory rested upon some unsupported hypothesis. I am convinced by this of how limited at bottom is our faith in theories; we regard them as instruments useful in discovery rather than actual demonstrations of fact [Perrin 1913 b, Para. 74].

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<sup>15</sup> Although Exner found that granular velocity decreased with larger particles and increased with rising temperature, when he calculated the granular kinetic energies from velocity measurements, the values came out dramatically smaller than those expected on the kinetic theory.

<sup>16</sup> Perrin realized the problem of measuring granular velocities at least by the time of the publication of his first experimental work on the Brownian movement in 1908. In his 1909 memoir he noted that velocities measured by Wiener, Ramsay, Exner, Zsigmondy, and himself were *grossly untrue* since “the entanglements of the trajectory are so numerous and rapid that it is impossible to follow them” [Perrin 1909 a, Para. 13].



**Three figures of granule displacements recorded by Perrin every 30 seconds. In *Les Atomes*, Perrin noted that for observations over one-hundredth the time, i.e. over 0.3 seconds, each segment would be replaced by a polygonal contour relatively as complex as the entire figure. This well shows that apparent velocity measurements are contingent on periods of observation and are therefore an ill-suited method of verifying the kinetic theory.**

Einstein also noticed the problem of measuring granular velocity in the Brownian movement and published a paper in 1907 to “facilitate for physicists who handle the subject experimentally the interpretation of their observations as well as the comparison of the latter with the theory” [Einstein 1907, p. 63]. He calculated the mean velocity for granules in colloidal platinum such as Svedberg had investigated and found the value was 8.6 cm/sec at a temperature of 292 Kelvin. However, he found that the velocity of such a granule would drop to a tenth of its original value in about  $3.3 \cdot 10^{-7}$  sec because of the very rapid viscous damping. Even though new impulses constantly counter the damping effect, the direction and magnitude of impulses are (approximately) independent of the original direction of motion and velocity of the particle; the granular motion varies in a

totally irregular manner. Einstein said, “It is therefore impossible – at least for ultramicroscopic particles – to ascertain [the mean velocity] by observations” [Einstein 1907, p. 66].

Einstein noted that an observer can never perceive the actual path traversed by a granule and a certain mean velocity will always appear to him as an instantaneous velocity. He ends the 1907 paper with this cautionary remark: “It is clear that the velocity ascertained thus corresponds to no objective property of the motion under investigation” [Einstein 1907, p. 67]. This became a major obstacle that Perrin had to overcome in order to compare the Brownian movement to the kinetic theory.

### *Distribution of granules in an emulsion – Equation II*

Perrin sidestepped the issue of accurately measuring granular velocity by taking an entirely different approach in confirming the kinetic theory of the Brownian movement. Van’t Hoff had extended the gas laws to dilute solutions, where osmotic pressure takes the place of pressure in the gaseous state. The extension held for all solutions that obeyed Raoult’s law.<sup>17</sup> Raoult’s law had been confirmed for small and large molecules including water (3 atoms), sugar (45 atoms), and quinine sulphate (over 100 atoms). Furthermore, experimental results on colloids strongly suggested the applicability of the theory of solutions to colloids and suspensions.<sup>18</sup> Perrin, realizing the

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<sup>17</sup> The theory of solutions was elaborated by Van’t Hoff and Walther Nernst as an analogue to the kinetic theory. Van’t Hoff published his extension of the gas laws to solutions in volume 1 of *Zeitschrift für physikalische Chemie*, which he co-edited with Wilhelm Ostwald, under the title *Stöchiometrie Verwandtschaftslehre* in 1887. Nernst published his work under the same title in volume 2 of the same journal in 1888.

<sup>18</sup> Nye provides a good summary of the relevant experimental work: “By the early twentieth century, it was shown that electrolytes which will precipitate a colloid, also diminish the osmotic pressure, and a dependence of osmotic pressure on temperature was also noted. It was accepted, then, by the end of the first decade of the twentieth century that the colloidal particles in some fashion cause the observed pressure” [Nye, p. 98].

analogy between the theory of solutions and the gas laws, extended the analogy to granules in an emulsion to obtain evidence in favor of the discreteness of matter. To Perrin, this was the basis of an *experimentum crucis* to do with the kinetic theory [Perrin 1913 b, Para. 53].<sup>19</sup>

In deriving his statistical law of equilibrium in emulsions of granules, Perrin derived an equivalent of the older Laplace function on the rarefaction of air with height. He obtained the following for the change in pressure from  $p$  to  $p'$  where  $M$  is the molar mass of the gas,  $h$  is the height difference from  $p$  to  $p'$ ,  $g$  is the acceleration due to gravity,  $R$  is the gas constant, and  $T$  is the absolute temperature:

$$\frac{p'}{p} = 1 - \frac{Mgh}{RT} \quad [1.3]$$

Perrin knew that the pressure halves for air after about 6 kilometers, halves for oxygen after about 5 kilometers, and halves for hydrogen after about 80 kilometers. Formula [1.3] suggested that the pressure would halve for any other gas based on its molar mass so long as the product  $M \cdot h$  remained constant. Perrin could test the formula for granules and, more importantly, he could directly weigh the granules instead of inferring their mass from the observed rarefaction. Before presenting his results, Perrin remarked:

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<sup>19</sup> From the original French: “J’ai cherché dans ce sens une expérience cruciale qui pût donner une base expérimentale solide pour attaquer ou défendre la théorie cinétique” [Perrin 1913 a, Para. 53].

Perrin believed that the extension of the gas laws to the Brownian movement was the basis of an *experimentum crucis* even before *Les Atomes*. An earlier such announcement by Perrin can be seen in a footnote to Para. 14 of his 1909 memoir *Brownian Movement and Molecular Reality*.

*We shall thus be able to use the weight of the particle, which is measurable, as an intermediary or connecting link between masses on our usual scale of magnitude and the masses of the molecules* [Perrin 1913 b, Para. 55].<sup>20</sup>

Since pressure is proportional to density and density is proportional to the number of granules, Perrin replaced  $\frac{p'}{p}$  by  $\frac{n'}{n}$ . Furthermore, since he could weigh individual granules, Perrin replaced the molar mass  $M$  by  $N \cdot m$ , where  $m$  is the mass of individual granules and  $N$  is Avogadro's number – the number of particles in a mole of something. Perrin also had to account for the upward thrust on the granules due to the intergranular liquid; the force is equal to  $m \cdot (\frac{d}{D}) \cdot g$  where  $D$  is the density of the granules and  $d$  is the density of the intergranular liquid. Perrin thus obtained his law on the vertical distribution of granules in equilibrium:

$$\frac{n'}{n} = 1 - \frac{N}{RT} m \left( 1 - \frac{d}{D} \right) gh \quad [2]$$

Perrin directly measured all the parameters in this equation except for  $N$ . As part of making convergent measurements of the granular mass  $m$ , he also confirmed Stokes' Law for grains falling in an emulsion, which was central to Einstein's theoretical derivations.<sup>21</sup>

Perrin measured parameters of the vertical distribution formula over a wide range of experimental conditions. He varied (1) the volumes of the granules in ratios of 1 to 50, (2) the intergranular liquid viscosities in ratios of 1 to 250, (3) the apparent density of the

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<sup>20</sup> From the original French: “*C'est ce poids du granule, encore mesurable, qui va faire l'intermédiaire, le relai indispensable, entre les masses qui sont à notre échelle et les masses moléculaires*” [Perrin 1913 a, Para. 55].

<sup>21</sup> At a May, 1908 meeting at the Académie des Sciences, Victor Henri contested that Stokes' law does not apply to small granules. Henri had conducted cinematographic studies to check Einstein's displacement formula and obtained results four times larger than the theoretical prediction. In questioning Stokes' law, Henri questioned Einstein's theoretical work.

granules in ratios of 1 to 5, (4) the temperature from  $-9^{\circ}\text{C}$  to  $60^{\circ}\text{C}$ , and (5) the granular material from gamboge to mastic [Perrin 1913 a, Para. 65]. Despite all this variation, the value of  $N$  consistently came out between  $65 \cdot 10^{22}$  and  $72 \cdot 10^{22}$ . Perrin found sufficient agreement between these values and the values derived from the kinetic theory to concede: “such decisive agreement can leave no doubt as to the origin of the Brownian movement” [Perrin 1913 b, Para. 65].

### *Diffusion of granules in an emulsion – Equations III, IV, and V*

Perrin began his Brownian movement studies without much knowledge of the theoretical work of Einstein and Smoluchowski.<sup>22</sup> In fact, Einstein had derived an alternative formulation of formula [2] as early as 1906. In his 2<sup>nd</sup> paper on the Brownian movement, Einstein came up with the probability distribution  $W$  of a granule along the height of an emulsion:

$$\partial W = \text{const} \cdot e^{\frac{-N}{RT} V(D-d)g\partial x} \partial x \quad [\text{Alternative form of 2}]^{23, 24}$$

Perrin saw an opportunity of further confirming the kinetic theory by investigating other features of the Brownian movement derived by Einstein, who brought together the study of diffusion with the study of fluctuation phenomena within the context of statistical

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<sup>22</sup> In a footnote to his 1909 memoir, Perrin noted that Einstein and Smoluchowski independently found the exponential distribution of granules in an emulsion and then acknowledged that he only learned about their work after his early experimental work of May 1908. Perrin goes on to say, “it does not seem to have occurred to them that in this sense an *experimentum crucis* could be obtained, deciding for or against the molecular theory of the Brownian movement” [Perrin 1909 a, footnote for Para. 14].

<sup>23</sup> I have substituted Perrin’s notation for Einstein’s where applicable. So, whereas Einstein used  $\rho$  and  $\rho_0$  for the granular and intergranular densities respectively, Perrin used  $D$  and  $d$  respectively. I will use Perrin’s notation throughout this paper.

<sup>24</sup> It is curious that Perrin, as well as other experimentalists, did not recognize the significance of Einstein’s 1905-06 theoretical work on the Brownian movement sooner. Both Nye and Brush speculate that this was probably because Einstein’s mathematical work was beyond the scope and understanding of even the most precocious experimentalist.

mechanics<sup>25</sup>. Max Born commented that confirmation of Einstein’s theory did “more than any other work to convince physicists of the reality of atoms and molecules, of the kinetic theory of heat, and of the fundamental part of probability in the natural laws”. Stephen Brush viewed it as the final blow from which the anti-atomistic “Energetics” movement never recovered [Brush, p. 2].

The first step in Einstein’s derivations was establishing a link between the bulk phenomenon of diffusion and the motion of individual molecules or granules. Working off of Van’t Hoff’s analogy between gases and solutions, he described the diffusion of granules by an osmotic pressure gradient.<sup>26</sup> He then applied Stokes’ law to describe the viscous force retarding the granular motion that maintains a dynamic equilibrium along the horizontal axis. By (1) viewing the dynamic equilibrium of granules as a balance between the force described by Stokes’ law and a process of diffusion and (2) utilizing the definition of the diffusion coefficient  $D$  as relating transport and density of particles, Einstein arrived at an expression for  $D$  in terms of atomic sizes:<sup>27</sup>

$$D = \frac{RT}{N} \times \frac{1}{6\pi a \xi} \quad [3]$$

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<sup>25</sup> Einstein developed his statistical mechanics in the most general way, and his methods did not depend on knowledge of the detailed interaction between the constituents of a system as in the case of the kinetic theory, where collision dynamics play a major role.

As of 1904, he considered radiation in thermal equilibrium the only system for which energy fluctuations could be observed. Einstein had derived an expression for mean square deviations from the average value of the energy spectrum of heat radiation. Renn speculates that Einstein may well have considered as early as 1904 that heat radiation may be conceived of as a collection of discrete light quanta [Renn p. 29-30].

<sup>26</sup> Einstein justified the analogy and its extension to granules by carrying out a short calculation with the help of his own statistical mechanical formulation to conclude, “as far as osmotic pressure is concerned, solute molecules and suspended particles are, according to [the molecular-kinetic theory of heat], identical in their behaviour at great dilution” [Einstein 1905, p. 9]. Brush notes that this calculation probably obscured the argument for most readers since the use of the phase integral had not yet become familiar [Brush, p. 19].

<sup>27</sup> Einstein’s approach as outlined here is taken primarily from Renn [Renn, p. 28-29].

where  $R$  is the gas constant,  $T$  is the absolute temperature,  $N$  is Avogadro's number,  $a$  is the granular radius, and  $\xi$  is the viscosity. Léon Brillouin, working under Perrin, tested this equation by observing the fixation of several thousand granules on an absorbing partition. For gamboge grains of equal size (radius of  $0.52\mu$ ) at  $38.7^\circ\text{C}$  in glycerin with a viscosity 165 times that of water at  $25^\circ\text{C}$ , Brillouin found a diffusion rate 140,000 times slower than that of sugar in water at  $20^\circ\text{C}$  and calculated  $N$  equal to  $69 \cdot 10^{22}$  with an imprecision of  $\pm 3$  percent, according to Perrin [Perrin 1913 b, Para. 78].

To describe the apparent motion of granules, Einstein brought formula [3] together with his work on fluctuation phenomena within the context of statistical mechanics. He took the familiar equation for diffusion:

$$\frac{\partial f}{\partial t} = D \frac{\partial^2 f}{\partial x^2}$$

and reinterpreted it as giving the probability distribution of individual granules based on his statistical mechanics. He described the irregular motion of granules, not in the ordinary sense along a continuous trajectory, but as a stochastic process governed by the function  $f(x,t)$  [Renn, p. 32]. Integrating over the function gave him the average displacement of a granule in the x-direction:

$$\lambda_x = \sqrt{x^2} = \sqrt{2Dt}$$

Substituting [3] for  $D$  in this equation gives the mean square of the displacement along the horizontal axis:

$$\frac{x^2}{t} = \frac{RT}{N} \times \frac{1}{3\pi a \xi} \quad [4]$$



Einstein ended his 1905 paper by saying, “It is to be hoped that some enquirer may succeed shortly in solving the problem suggested here, which is so important in connection with the theory of Heat” [Einstein, p. 18].

Einstein’s wish was soon fulfilled, but not before some problems of verification were encountered by Victor Henri and Svedberg. Svedberg attempted verification of Einstein’s theory in 1906 but found displacements 6 or 7 times too great. Victor Henri, as mentioned above, found values that were still 4 times too great. The first of the confirmations came from Seddig who took two photographs of aqueous suspensions of cinnabar on the same plate at an interval of 0.1 seconds and measured the distance of corresponding images on the plate.<sup>28</sup> He found that the displacements at different temperatures were inversely proportional to the viscosities, as per theory. Henri, in contrast, at least confirmed the proportionality of  $x^2$  to  $t$ , but his results were quantitatively discrepant.

Chaudesaigues, working under Perrin, followed the movements of single particles of gamboge under the microscope and recorded their positions at equal time intervals. In a November, 1908 paper he reported that Einstein’s formula is *exact* when  $N$  is equal to  $64 \cdot 10^{22}$ . Perrin had overseen seven series of experiments on Einstein’s displacement formula by the time of *Les Atomes* and found  $N$  between  $55 \cdot 10^{22}$  and  $80 \cdot 10^{22}$ . Perrin cautions in the text that the temperature was unknown for the series yielding  $N$  as  $55 \cdot 10^{22}$  [Perrin 1913 b, Para. 75]. In his most careful series, he found  $N$  as  $64 \cdot 10^{22}$ .

Perrin also verified Einstein’s derivation of rotational Brownian movement:

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<sup>28</sup> From the *Notes* accompanying Einstein’s five papers on the Brownian movement from 1905 to 1908 [Fürth, pp. 102-104].

$$\frac{A^2}{t} = \frac{RT}{N} \times \frac{1}{4\pi a^3 \xi} \quad [5]$$

where  $A^2$  is the mean square of the component of the angle of rotation about a given axis or the third of the mean square of the angle of rotation in time  $t$ . Perrin mentions in *Les Atomes* that the rotational motion of granules had not been made the subject of experimental study before him, and he had to overcome a few difficulties before testing the formula. The mean rotation of granules that he had been working with to test [2] would be too rapid to be perceived. Perrin overcame this problem by preparing very large granules of gamboge and mastic that were 70,000 times greater in mass than the smallest granules studied in the determination of the vertical distribution [Perrin 1913 b, Para. 76]. Perrin also had to make sure the granules contained inclusions so that the rotation could be perceived; at the same time, he had to ensure that the inclusions did not appreciably affect the granular density. From 200 observations of gamboge grains (diameter of  $13\mu$ ), Perrin found  $N$  as  $65 \cdot 10^{22}$ .

The verification of [4] and [5] implies equality between translation and rotational Brownian movements. This equipartition of energy is famously attributed to Boltzmann, but had been proposed and elaborated by James Waterston as early as 1845. In *A History of Random Processes: Brownian Movement from Brown to Perrin*, Brush refers to the equipartition theorem as the Waterston-Maxwell equipartition theorem but, other than that, Waterston's contributions are mostly forgotten. The Royal Society denied Waterston publication in 1845 on the basis that his work was too speculative.<sup>29</sup> In any case, Perrin verified the equipartition theorem in the translational and rotational motion of granules.

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<sup>29</sup> Truesdell remarks, "In 1845 physicists believed either that heat is a fluid which can pass through continuous matter, or that heat is a vibratory motion of molecules. They did not wish to

Perrin confirmed the Brownian movement against other tenets of the kinetic theory as well. Chaudesaigues working under Perrin confirmed the statistical distribution law<sup>30</sup> in the distribution of horizontal displacements of 500 granules to directly verify another central tenet of the kinetic theory in the Brownian movement. The numerical convergence of Avogadro's number confirmed that the gas laws rigorously apply to emulsion, and direct verification of the tenets of the kinetic theory in the Brownian movement was expected after the numerical convergence. Perrin concluded his Brownian movement presentation by saying:

The laws of the perfect gases are thus applicable in all their details to emulsions. This fact provides us with a solid experimental foundation upon which to base the molecular theories [Perrin 1913 b, Para. 79].

### *Diffusion of light in mediums – Equations VI and VII*

Diffusion of light in a medium was a new phenomenon, absent from Perrin's 4<sup>th</sup> paper in 1908,<sup>31</sup> that he included in *Les Atomes*. Perrin adopted Smoluchowski's

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think about other possibilities". He then quotes the two referees who assessed Waterston's 1845 paper – the first referee did not think it worthy to be published in the *Philosophical Transaction* and the other wrote, "the paper is nothing but nonsense, unfit even for reading before the Society" [Truesdell, p. 295].

Waterston's paper was finally unearthed in 1891 by Lord Rayleigh from the Royal Society archives and he caused it to be published in 1893 in *Philosophical Transactions*. Rayleigh gave the paper a short introduction, adding the counsel, "highly speculative investigations, especially by an unknown author, are best brought before the world through some other channel than a scientific society..." and "a young author who believes himself capable of great things would usually do well to secure the favourable recognition of the scientific world by work whose scope is limited, and whose value is easily judged, before embarking upon higher flights" [Truesdell, p. 296].

<sup>30</sup> This law specifies how frequently granules would be expected to be displaced along the x-axis by certain amounts over a given time. According to this law, the displacement of granules is Gaussian distributed about its mean with variance equal to  $2 \cdot D \cdot t$ , where  $D$  is the coefficient of diffusion and  $t$  is the time.

<sup>31</sup> In *Grandeur des molecules et charge de l'électron*, Perrin's 4<sup>th</sup> paper in 1908, he reviews outstanding efforts to measure Avogadro's number. He includes measurements from (1) the kinetic theory, (2) from electrolysis combined with the elementary charge, and (3) black-body

derivation of the mean square of density fluctuations in a liquid by (1) application of Rayleigh's theory on the intensity of light diffused by a small particle of different refractive index than the medium and (2) substitution of variation in density for variation in refractive indices. By summing all the intensities of laterally diffused light due to all the small sections composing a liquid, the net intensity of light comes out as:

$$i = \frac{\pi^2}{18} \cdot \frac{1}{\lambda^4} \cdot \frac{RT}{N} \cdot (\mu_o - 1)^2 (\mu_o + 2)^2 \cdot \frac{1}{-v_o \cdot \frac{\partial p}{\partial v_o}} \quad [6]$$

where  $\lambda$  is the wavelength of the incident light (in *vacuo*),  $R$  is the gas constant,  $T$  is the absolute temperature,  $N$  is Avogadro's constant,  $\mu_o$  is the mean refractive index of the fluid,  $v_o$  is its specific volume, and  $\frac{\partial p}{\partial v_o}$  is its isothermal compressibility.

All the quantities in [6] were measurable except for  $N$ . A convergent value of  $N$  would support Smoluchowski's theory as well as its extension to the lateral diffusion of light in liquids by Keesom. Measurements by Kamerlingh Onnes and Keesom in ethylene gave a value for  $N$  as  $75 \cdot 10^{22}$  with an imprecision of  $\pm 15$  percent, according to Perrin [Perrin 1913 b, Para. 82]. Moreover, on the assumption that density fluctuations in liquids are due to variations in the number of molecules per unit volume and the supposition that we can count the number of these molecules in unit volume at STP, the calculated value of  $N$  is comparable to the values from the kinetic theory and the Brownian movement.

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radiation. He also mentions, in a footnote, Rutherford's August 1908 memoir where  $N$  was calculated as  $62 \cdot 10^{22}$  and  $72 \cdot 10^{22}$  from two groups of measurements based on the half-life of radium. Of course, the premier method was Perrin's own, of which he said, "me semble *directe et susceptible d'une précision illimitée*."

Smoluchowski's theory of fluctuations could be further extended to gases by supposing that the composition of air is homogeneous<sup>32</sup>, so that variation in refraction is due to density variations and not composition differences. Using Boyle's law and the fact that the refractive index of air is very nearly one, equation [6] becomes for gases:

$$i = \frac{\pi^2}{2\lambda^4} \cdot \frac{RT}{N} \cdot (\mu_o^2 - 1)^2 \cdot \frac{1}{p}$$

The  $(\mu_o^2 - 1)^2$  factor is very small because of the feeble refractive power of gases, but the total light diffused by a large volume can be better perceived. Finding the diffusion of light by a large volume was the idea behind measuring  $N$  based on the blueness of the sky. The idea is that laterally diffused light is polarized in the plane passing through the incident sunbeam and the eyes of the observer. Light of shorter wavelength undergoes greater diffraction, and assuming that light is diffracted by individual molecules, the intensity of direct solar radiation to the intensity of the light diffused by the sky is:

$$\frac{e}{E} = \pi^3 \omega^2 M \cdot \frac{p}{g} \cdot \frac{1 + \cos^2 \beta}{\cos \alpha} \cdot \left( \frac{\mu^2 - 1}{d} \right)^2 \cdot \frac{1}{\lambda^4} \cdot \frac{1}{N} \quad [7]$$

where  $e$  and  $E$  are illuminations obtained in the field of an objective pointed towards a portion of the sky and the sun respectively,  $\omega$  is the apparent semi-diameter of the sun,  $M$  is the molar mass of air,  $p$  and  $g$  are the atmospheric pressure and the acceleration due to gravity at the point of observation,  $\alpha$  is the zenith distance to the point of observation of the sky making an angle  $\beta$  with incident solar rays,  $\frac{\mu^2 - 1}{d}$  is the refractive power of air,  $\lambda$  is the magnitude of each wavelength, and  $N$  is Avogadro's number.

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<sup>32</sup> The assumption of homogeneity allows uniform refraction by components. Perrin considered this assumption "sensibly the case for air" [Perrin 1913 b, Para. 83].

Lord Kelvin was the first to obtain estimates for  $N$  based on Sella's experimental work at the summit of Monte Rosa. He found  $N$  between  $30 \cdot 10^{22}$  and  $150 \cdot 10^{22}$ . In *Les Atomes*, Perrin cites the then new experimental results of Fowle, which gave  $N$  as  $65 \cdot 10^{22}$  once corrected for the anisotropy of air molecules.

### *Black body radiation – Equation VIII*

Lummer and Pringsheim reported the frequency distribution of radiation from the first experimental black cavity in early February 1899. Wien's distribution law approximated these measurements, but an apparent dependence of the two constants in the law on the temperature and wavelength was noticed. More experimental work in March 1900 proved that Wien's distribution law was inadequate.<sup>33</sup> Planck sought to provide an adequate representation of the experimental work, which led to what he called, "a few weeks of the most strenuous work of my life".

In October, 1900, Planck announced his distribution law, which agreed with all new observations.<sup>34</sup> He referred the specific intensity of a monochromatic ray to its wavelength and obtained the expression:

$$E_{\lambda} = \frac{8\pi ch}{\lambda^5} \cdot \frac{1}{e^{\frac{ch}{k\lambda T}} - 1} \quad [8]$$

In December 1900, Planck announced that the value of both universal constants  $h$  and  $k$  may be calculated with the aid of available measurements. Measurements by Ferdinand Kurlbaum on the total energy radiating into air from 1 sq. cm. of a black body gave:

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<sup>33</sup> This history is taken from Kuhn's *Black-body theory and the quantum discontinuity: 1894-1912*, pp. 92-113.

<sup>34</sup> Kuhn comments that right after its introduction, new measurements quickly showed equation [8] to be superior to preexisting distribution laws. After the resolution of a few anomalies, it has agreed with observations ever since [Kuhn, pp. 97].

$$\frac{k^4}{h^3} = 1.1682 \cdot 10^{15}$$

Lummer and Pringsheim determined the product  $\lambda \cdot \theta$ , where  $\lambda_m$  is the wavelength of maximum energy in air at temperature  $\theta$ , to be 2940 micron·degree. Setting the derivative of  $E$  with respect to  $\theta$  in equation [8] equal to 0, Planck found:

$$\frac{h}{k} = 4.866 \cdot 10^{-11}$$

Based on these measurements, Planck announced the value of the two constants:

$$k = 1.346 \cdot 10^{-16} \frac{\text{erg}}{\text{deg}}$$

$$h = 6.55 \cdot 10^{-27} \text{ erg} \cdot \text{sec}$$

Planck rewrote Boltzmann's definition of entropy to show that for a gas in equilibrium with radiation, the total entropy could be the sum of the entropy of the parts only if  $k$  were equal to  $\frac{R}{N}$  [Kuhn, p. 111]. Boltzmann's constant acted as the gas constant per molecule of gas and  $R$  was well known from the ideal gas law. The quotient of  $R$  to  $k$  gave Planck a value of  $N$  as  $62 \cdot 10^{22}$ .

### *Measurement of the elementary charge – Equation IX*

The measurement of the elementary charge was an effort initiated by J.J. Thomson in 1897 and realized by Millikan to four significant figures by 1913. It was a route to the determination of  $e$  independent from electrolysis studies. In electrolysis studies, conducted by Michael Faraday, the amount of charge required to electrolyze one mole of various monovalent ionic compounds comes out as a constant value. This constant value became known as the Faraday constant and was known since the 1830s. Since the number of molecules in a mole is equal to Avogadro's number, the comparison

of the Faraday constant to the elementary charge should give the number of molecules that make up one mole of a monovalent ionic compound:

$$\frac{F}{e} = N \quad [9]$$

This equation presupposes that there is a unique elementary charge and that all charges are composed of integral multiples of it. This was the crucial assumption verified by Millikan in his oil-drop experiments in 1911.<sup>35</sup> It validated that the Faraday is an integral multiple of the elementary charge that is released when a mole of a monovalent ionic compound is electrolyzed. So long as each unit of charge is linked to its own unit of mass that is released during electrolysis, we have grounds to suppose that matter is discrete. We can count these discrete particles by comparing the Faraday to the elementary charge.

The value of the Faraday constant, as mentioned, had been established for quite some time<sup>36</sup>; but the value of the elementary charge  $e$  was still disputed leading up to *Les Atomes*. In *Brownian Movement and Molecular Reality*, Perrin used the value of  $e$  from experimental work by Ehrenhaft ( $4.6 \cdot 10^{-10}$  esu) and Maurice de Broglie ( $4.5 \cdot 10^{-10}$  esu) to give  $N$  as  $64 \cdot 10^{22}$ . In the 1910 English translation, the translator Frederick Soddy commented in a footnote about the determination of  $e$  by Millikan from individual drops balanced in an electric field. He considered this an *improved* experiment, from which  $e$  was calculated as  $4.65 \cdot 10^{-10}$  esu and  $N$  as  $62 \cdot 10^{22}$  [Perrin 1909, p. 84]. The measurement

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<sup>35</sup> Millikan's value for  $e$  changed from 1911 ( $4.89 \cdot 10^{-10}$  esu) to 1913 ( $4.774 \cdot 10^{-10}$  esu) and even his 1913 value was incorrect due to a systematic error in his viscosity of air value. This, however, did not contradict his original finding that there is a unique elementary charge and all charges are composed of integral multiples of it. The changing value meant that  $e$  had a different value than previously supposed, but the elementary charge remained unique and discrete throughout.

<sup>36</sup> In his 1913 revaluation of  $e$ , Millikan commented, "The value of the Faraday constant has now been fixed virtually by international agreement at 9,650 absolute electromagnetic units" [p. 140].



of individual drops became the preferred way to measure  $e$ , but corrections to Stokes' law to find the mass of the drops were disputed even at the time of *Les Atomes*.

In *Les Atomes*, Perrin gives his preferred value of  $N$  as  $67 \cdot 10^{22}$  from the quotient of the Faraday constant to the elementary charge. His value of  $e$  differed from Millikan's preferred value of  $e$ , which gave  $N$  as  $60 \cdot 10^{22}$ . Despite the difference, both values were close to the values of  $N$  obtained from other methods. The values of  $N$  based on  $e$  from experimental work by Ehrenhaft, de Broglie, Millikan, and Jules Roux, working under Perrin, fit into the  $60 \cdot 10^{22}$  to  $75 \cdot 10^{22}$  range from the kinetic theory, the Brownian movement of granules, the diffusion of light in apparently homogenous mediums, and the theory of black body radiation. The value of  $N$  from  $e$  had an added virtue, however: this indirect method implied discreteness of matter to the extent that it showed that the elementary charge is discrete. This will be worth looking into in the next chapter on the details of the experiments that imply discreteness.

### *Radioactivity – Equations X, XI, XII, and XIII*

The determination of  $N$  from radioactivity was a prominent feature in *Les Atomes* compared to Perrin's passing remark about it in *Grandeur des molecules et charge de l'électron*. In fact, Perrin gave four different equations from radioactivity phenomena to find  $N$  based on (1) the charge of alpha particles, (2) the amount of helium produced during radium decay, (3) the amount of radium lost in decay, and (4) the energy radiated by radium in the form of alpha particles. (1) to (4) give the following equations respectively:

$$\frac{q}{n} = 2e = \frac{2F}{N} \quad [10]$$

where  $q$  is the net charge on  $n$  alpha particles passing into a Faraday cylinder per second.  $2e$  is the charge on each alpha particle, equal to two elementary charges. The comparison of  $e$  obtained this way to the faraday constant gave another calculation of  $N$ .

$$\frac{n \cdot 86400 \cdot 465}{V_{He}} \cdot 22400 = N \quad [11]$$

where  $n$  is the number of alpha particles emitted by a gram of radium per second,  $V_{He}$  is the volume of helium produced per year by radium decay in cubic millimeters, 22400 is the volume occupied by a mole of a gas at STP in cubic millimeters, and  $N$  is Avogadro's number.

$$M_{Ra} \cdot n = N \cdot f_{lost} \quad [12]$$

where  $M_{Ra}$  is the molar mass of radium,  $f_{lost}$  is the fraction lost from a mole of radium in one second, and  $n$  and  $N$  are the same as above.

$$\frac{1}{2} \cdot \frac{4}{N} \cdot n \cdot (v_1^2 + v_2^2 + v_3^2 + v_4^2) = \frac{C_{Ra} \cdot 4.18 \times 10^7}{3600} \quad [13]$$

where the left side of the equation represents the kinetic energy of alpha particles emitted in the first second; the right side of the equation represents the heat liberated by radium in decay in the first second;  $\frac{4}{N}$  is the mass of one helium atom;  $v_1$ ,  $v_2$ ,  $v_3$ , and  $v_4$  are initial velocities of the four series of alpha projectiles emitted by radium in radioactive equilibrium;  $C_{Ra}$  is the heat liberated per gram of radium per hour in calories;  $4.18 \times 10^7$  is the conversion factor from calories to joules; and  $n$  and  $N$  are the same as above.

In *Les Atomes*, Perrin cites  $N$  as  $62 \cdot 10^{22}$ ,  $62 \cdot 10^{22}$ ,  $71 \cdot 10^{22}$ , and  $60 \cdot 10^{22}$  from these four methods respectively. The important step in these determinations of  $N$  was equating alpha particles with helium ions emitted or radium atoms lost. Rutherford, working with Royds, had given convincing evidence for these claims by 1909. The experiments on

radioactivity linked another phenomenon to the convergent determination of Avogadro's number. Moreover, just like measurement of the elementary charge, these determinations had the virtue that they implied discreteness of matter to the extent the experiments showed that the alpha particles emitted per second were discrete units.

### **Assigning meaning to $N$**

#### *The stability of $N$*

The stability of  $N$  within a phenomenon at least construed it as a constant of proportionality. If various experimental parameters are varied and  $N$  still has the same value in any one indirect measurement, this counts as a stable measurement. The strongest support for this came from Perrin's experimental work on the vertical distribution of granules in emulsions, where he varied the granular material from gamboge to mastic and significantly varied experimental parameters of granular volumes, viscosities, apparent granular densities, and temperature. Yet,  $N$  consistently came out between  $65 \cdot 10^{22}$  and  $72 \cdot 10^{22}$ . Millikan's determination of  $e$  also gave a stable value of  $N$  from ions containing the elementary charge or multiples of it. The measurement spanned ions carrying charges that were to  $e$  as 1, 2, 3, 4, 5, and so on.

Millikan studied oil droplets, and previous determinations had been made on tobacco-smoke and water vapor as well. The method of oil drops was superior to other methods because oil drops were effectively spherical and did not evaporate. The sphericity allowed the application of Stokes' law to determine the mass of the droplet. Even if Stokes' law did not perfectly apply in gases, corrections could be systematically made to spherical droplets in a way that was not tractable for irregularly shaped droplets. Tobacco-smoke was not spherical, and water vapor evaporated, which meant that its mass kept changing. The calculation of  $e$  was most tractable using oil droplets, but

measurements using other materials still gave comparable values of  $N$ . Even though experimental parameters were not varied as much as they were in the Brownian movement experiments,<sup>37</sup> the various determinations of  $e$  also suggested a stable value for  $N$ .

Other experiments also supported a stable value for  $N$ . Experimental work on the horizontal displacement of granules instantiated an increasingly stable value for  $N$  over time; Perrin had conducted seven series of experiments by the time of *Les Atomes*. Even in experiments lacking range on their parameters, a stable value for  $N$  in repeated measurements was meaningful because it showed that the measurement outcome was not arbitrary. A measurement procedure must always have some outcome, even if that outcome has no real meaning; but repeated measurements can decide whether a measured value is arbitrary or stable. This was the source of at least some support for the stability of  $N$  based on viscosity measurements of monatomic argon. Argon is one of the rare gases whose molecules – i.e. atoms – approximate a sphere, and thereby most accords with the tenets of the kinetic theory to calculate  $N$  from viscosity measurements. Even though there are not many other gases the molecules of which approximate a sphere, the same viscosity for argon from repeated measurements was support for the stability of  $N$ .

The stability of  $N$  in the various phenomena gave evidence that it was a constant of proportionality in the equations of those phenomena. At the very least,  $N$  was as a link between the various parameters of an equation. It was assigned a value based on experimental results from repeated measurements, over a range of conditions. Moreover,

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<sup>37</sup> In fact, the parameters that could be manipulated in the Brownian movement experiments – temperature, granular mass, granular densities – either did not influence the measurement of  $e$  or were not easily manipulable.

$N$  linked the parameters of several equations. Stable values for  $N$  were found across phenomena, and this was a major point in *Les Atomes*.

### *The convergence of $N$*

Perrin summarized the experimental work he discusses in *Les Atomes* by giving results for  $N$  from each measurement. For all the equations, the results were as follows:

$$N\pi D^2 = \frac{V}{L\sqrt{2}} \quad [1.1] \quad \text{and} \quad \left(P + \frac{A}{V^2}\right) \cdot (V - 4B) = RT \quad [1.2] \quad N = 62 \cdot 10^{22}$$

$$\frac{n'}{n} = 1 - \frac{N}{RT} m \left(1 - \frac{d}{D}\right) gh \quad [2] \quad N = 68 \cdot 10^{22}$$

$$D = \frac{RT}{N} \times \frac{1}{6\pi a \xi} \quad [3] \quad N = 69 \cdot 10^{22}$$

$$\frac{x^2}{t} = \frac{RT}{N} \times \frac{1}{3\pi a \xi} \quad [4] \quad N = 64 \cdot 10^{22}$$

$$\frac{A^2}{t} = \frac{RT}{N} \times \frac{1}{4\pi a^3 \xi} \quad [5] \quad N = 65 \cdot 10^{22}$$

$$i = \frac{\pi^2}{18} \cdot \frac{1}{\lambda^4} \cdot \frac{RT}{N} \cdot (\mu_o - 1)^2 (\mu_o + 2)^2 \cdot \frac{1}{-v_o \cdot \frac{\partial p}{\partial v_o}} \quad [6] \quad N = 75 \cdot 10^{22}$$

$$\frac{e}{E} = \pi^3 \omega^2 M \cdot \frac{p}{g} \cdot \frac{1 + \cos^2 \beta}{\cos \alpha} \cdot \left(\frac{\mu^2 - 1}{d}\right)^2 \cdot \frac{1}{\lambda^4} \cdot \frac{1}{N} \quad [7] \quad N = 65 \cdot 10^{22}$$

$$E_\lambda = \frac{8\pi ch}{\lambda^5} \cdot \frac{1}{e^{\frac{ch}{k \cdot \lambda \cdot T}} - 1} \quad [8] \quad N = 62 \cdot 10^{22}$$

$$\frac{F}{e} = N \quad [9] \quad N = 67 \cdot 10^{22}$$

$$\frac{q}{n} = 2e \quad [10] \quad N = 62 \cdot 10^{22}$$

$$\frac{n \cdot 86400 \cdot 465}{V_{He}} \cdot 22400 = N \quad [11] \quad N = 62 \cdot 10^{22}$$

$$M_{Ra} \cdot n = N \cdot f_{lost} \quad [12] \quad N = 71 \cdot 10^{22}$$

$$\frac{1}{2} \cdot \frac{4}{N} \cdot n \cdot (v_1^2 + v_2^2 + v_3^2 + v_4^2) = \frac{C_{Ra} \cdot 4.18 \times 10^7}{3600} \quad [13] \quad N = 60 \cdot 10^{22}$$

These results gave evidence that  $N$  is a universal constant of proportionality. It links not just the parameters of one phenomenon but links parameters across many phenomena.

The convergence of  $N$  across phenomena was indeed remarkable. Perrin realized this as early as 1909:

What brings out in some ways what is now tangible in molecular reality, is to compare two laws in which Avogadro's constant enters. The one expresses this constant in terms of certain variables,  $a, a', a'', \dots$ ,

$$N = f[a, a', a'' \dots];$$

the other expresses it in terms of other variables,  $b, b', b'', \dots$ ,

$$N = g[b, b', b'' \dots].$$

Equating these two expressions we have a relation *where only evident realities enter*, and which express a profound connection between two phenomena at first sight completely independent, such as the transmutation of radium and the Brownian movement [Perrin 1909 a, p. 91-92].

This passage is often used to support that Perrin's experimental work and the convergence of Avogadro's number across phenomena did not establish molecular reality.<sup>38</sup> However, Perrin certainly did not think this because in that very passage he says that *molecular reality* links different phenomena. At the same time, this passage perhaps shows that the connection between phenomena does not necessitate discrete molecules and atoms as the connecting link. Convergence establishes  $N$  as a universal constant of proportionality, but does not necessitate that it is an integer. Perrin explicitly argued for the discreteness claim at various points in *Les Atomes* and especially focused on results

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<sup>38</sup> Bas van Fraassen remarks that this passage by Perrin suggests the importance of the standards of *Determinability* and *Concordance* that must be met to establish a constant, such as  $N$  [van Fraassen, p. 21-22]. However, Perrin did not leave the significance of  $N$  at that. Elsewhere he argued that its measurements establish the discreteness of matter, which van Fraassen does not mention.

from the Brownian movement. If the argument for discreteness were based merely on numerical convergence, nothing would have substantially distinguished Perrin's 1913 results from Lord Kelvin's 1870 results.

### *N as an integer*

There is more to establishing the discreteness of matter, then, than just numerical convergence. Convergence of  $N$  from measurements of thin gold-foils with the kinetic theory is not as meaningful as that from measurements of displacements and distributions of granules in emulsions. Discreteness must be found in the details of the experiments. This is not to say that discreteness was evident in all measurements that Perrin mentions in *Les Atomes*. In studies of black-body radiation,  $N$  is calculated from  $R$  and  $k$ , which are both real numbers to many decimal places. To suppose that their quotient is an integer is not obvious, though, and is even counterintuitive. Support for  $N$  being an integer is found only in some of the experiments. I will discuss them in the rest of this paper.

To claim that  $N$  is an integer is equivalent to claiming discreteness. Support for these claims was found in (1) the measurement of  $e$  and its comparison to the Faraday constant, (2) the measurement of alpha particles in radioactive studies, and (3) the measurement of granules in the Brownian movement.  $N$  was measured indirectly in the first two studies by measuring a variable  $V$ . If  $V$  was clearly discrete, then so was  $N$ . In the Brownian movement studies,  $N$  was measured directly from discrete granules.

The variable in electrochemical studies was the elementary charge. The measurement of  $e$  supported that the elementary charge is discrete, unique, and that all charges come in integral multiples of it. The Faraday is an integral multiple of the elementary charge obtained from the electrolysis of one mole of a monovalent ionic

compound. So long as each unit of charge is linked to its own unit of mass that is released during electrolysis, a mole of a monovalent ionic compound is an integral multiple of discrete molecules that collectively liberate a Faraday's worth of elementary charges upon electrolysis.

The variable in radioactivity studies was the alpha particle. The counting of alpha rays by scintillation techniques or using a Geiger counter supported that they consisted of discrete alpha particles. Deflection studies of alpha particles showed that they were uniquely discrete. An aggregate of these particles then is a collection of discrete particles, and  $N$  found from their comparison represents discrete molecules.

Building on from this, the Brownian movement supported discreteness based on the discreteness of granules. The granules were visibly discrete. In addition to this, the Brownian movement was an extension of molecular movement.

Discreteness is indirectly or directly implied in these three experiments. It will be worthwhile to look at these experiments in detail. First, I will discuss the indirect measurements from the elementary charge and alpha particles in Chapter III. I will then discuss the Brownian movement in Chapter IV.



### III: Discreteness in Indirect Phenomena

#### **The Range on $N$ as of 1913**

By 1913, Perrin had brought together thirteen different equations with different parameters to measure Avogadro's number in *Les Atomes*.<sup>39</sup> This bringing together of convergent measurements of  $N$  is typically considered the crux of the argument for the discreteness of matter. This consideration goes alike for supporters and protestors of the argument for discreteness. The former group includes Wesley Salmon, who finds a *clear-cut form of argument* in *Les Atomes* based on the convergence of  $N$  from entirely different methods [Salmon, p. 216]. The latter group includes Bas van Fraassen, who sees the convergence of  $N$  between Perrin's results on the vertical distribution of granules and Einstein's theoretical derivations as merely a *gratifying aspect* of Perrin's research that still did not provide evidence for molecular reality.<sup>40</sup>

The convergent measurement of a parameter was not new to Perrin. Huygens had complementary measurements for surface gravity by 1659. J.J. Thomson found complementary measurements for  $e/m$  in 1897 that others made precise over the next six to ten years. The speed of light had been measured both directly and indirectly from measured electromagnetic constants by the end of the 19<sup>th</sup> century. Perrin's compilation contrasted with these earlier instances of convergence in the breadth of phenomena converging on  $N$ , which was quite impressive. At the same time, the convergence was not

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<sup>39</sup> See Perrin's tabulation in Para. 119 of *Les Atomes* or a similar representation in Chapter II of this paper on p. 36.

<sup>40</sup> Bas van Fraassen does not say this explicitly but implies it: "It is still possible, of course, to also read these results as providing evidence for the reality of molecules. But it is in retrospect rather a strange reading..." [van Fraassen, p. 22]. Interestingly, van Fraassen does not say anything about the other eleven independent methods to calculate  $N$  that Perrin had tabulated by 1913. I presume he would say the same thing – that taking the convergence of  $N$  across phenomena as evidence for the reality of molecules is rather a strange reading or an unjustified inference.

perfect or even remotely comparable to the four significant figure agreement Huygens obtained for surface gravity. The value of  $N$  from different measurements varied between  $60 \cdot 10^{22}$  and  $75 \cdot 10^{22}$  with Perrin's preferred value at  $68 \cdot 10^{22}$ ; the recommended value listed by CODATA in 2010 was  $6.022\,141\,29(27) \times 10^{23}$ .

Perrin and his contemporaries were clearly not looking for four significant figure agreement of  $N$  across phenomena. Even with a range from  $60 \cdot 10^{22}$  to  $75 \cdot 10^{22}$ , Perrin happily announced:

Seeing that not only is the same magnitude obtained by each method when the conditions under which it is applied are varied as much as possible, but that the numbers thus established also agree among themselves, without discrepancy, for all the methods employed, the real existence of the molecule is given a probability bordering on certainty [Para. 119].

Wesley Salmon has rightly pointed out that, given the difficulty of the experiments and measurement uncertainty, we should not set too high a standard for uniformity [Salmon, p. 224]. He sets the following standard: "Let us say that values lying between  $4 \cdot 10^{23}$  and  $8 \cdot 10^{23}$  are acceptable". This only pushes the problem back, however, for the question of what standard to set is replaced by how to set that standard.

## **Standards of Convergence**

### *Convergence in Perrin's 1913 results*

As was hinted above, dealing with convergence confronts us with at least two tasks: (1) determining what counts as convergence and (2) determining how much convergence is satisfactory to establish a certain claim. Answers to these questions are not obvious. It is not obvious whether Perrin's results for  $N$  from  $60 \cdot 10^{22}$  to  $75 \cdot 10^{22}$  were convergent or satisfactory to establish the discreteness of matter.

One way to assess convergence is by seeing how much different measurement results overlap within their probable error bands. Each measurement result has more or less error associated with it. In *Les Atomes*, Perrin attributed a 30 percent error to the measurement result for Avogadro's number based on viscosity measurements of gases within the context of kinetic theory. He attributed the error to approximations made in deriving the Clausius-Maxwell and van der Waals equations [Perrin 1913 b, Para. 49]. In contrast, Millikan attributed a 1 in 2,000 error to his determination of the elementary charge as  $4.89 \cdot 10^{-10}$  esu before Perrin published *Les Atomes*. In 1913, Millikan came up with a different value of  $4.774 \cdot 10^{-10}$  esu, this time with an error of 2 in 1,000.<sup>41</sup> The change in the new value of  $e$  turned out around forty-five times the estimated error from the old value. Even the new value of  $e$ , which Millikan still quoted in his 1917 memoir *The Electron*, is off by three times the 2 in 1,000 estimate when compared to the accepted value today.<sup>42</sup> Millikan's  $4.774 \cdot 10^{-10}$  value was in error due to an incorrect value for the viscosity of air, which led to a systematic error. This systematic error was not exposed by variance in Millikan's measured values, the basis for his error-bound estimates.

Systematic errors are found by comparing the results from different methods of measurement and looking for what is responsible for discrepant results, if there are any. In the case of a well-defined constant, systematic errors in discrepant measurements can be searched by comparison to the methods that provide a well-defined value.  $N$ , however, was not well-defined as of 1913, so that for a long time, the measurement of  $e$  – with its

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<sup>41</sup> Millikan calculated this error based on the square root of the sum of the squares of uncertainties in four continuous factors to find  $e$ . He compared this to his earlier value of  $4.891 \cdot 10^{-10}$  esu and attributed the significant change to systematic changes in the three factors  $\eta$ ,  $A$ , and  $d$  to find  $e$  [Millikan 1913, p. 140-141].

<sup>42</sup> Millikan even decreased the probable error to 1 in 1000 by 1917 [Millikan 1917, p. 119].

four significant figure precision – was the preferred way of calculating  $N$  from the Faraday constant.<sup>43</sup> The probable error of 2 in 1,000 did not account for the erroneous viscosity of air measurement. Comparison of different measurement results for  $N$  with probable errors would have left the issue of systematic errors unaddressed as of 1913. Results for  $N$  from studies of the Brownian movement and opalescence clustered around  $68 \cdot 10^{22}$  whereas results from electrochemistry, black-body radiation, and radioactivity mainly clustered around  $60 \cdot 10^{22}$ . The Brownian movement experiments most convinced scientists, notably Ostwald, about molecular reality, whereas experiments from electrochemistry, black-body radiation, and radioactivity were more precise.

There was no obvious way to reconcile the range from  $60 \cdot 10^{22}$  to  $75 \cdot 10^{22}$  into a better-defined value for  $N$ , and the question whether  $N$  is an integer thus remained open. Wesley Salmon has argued that convergence of  $N$  across phenomena was still strong support that molecular reality is the connecting link between phenomena.<sup>44</sup> He appeals to Reichenbach's principle of the common cause in terms of the statistical structure of a conjunctive fork to model the argument for discreteness. For two results A and B with a common causal antecedent, the notation is as follows:

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<sup>43</sup> In 1929, the “Millikan value of  $e$ ” ( $\sim 4.77 \cdot 10^{-10}$  esu) contrasted with another value ( $\sim 4.80 \cdot 10^{-10}$  esu) obtained by means of the wavelengths of x-rays, as measured with rule gratings. Over the next few years, extensive experimental and theoretical work made it quite clear that the rule-grating value for  $e$  was essentially correct, and Millikan's value was in error due to an incorrect measurement of the viscosity of air [Birge, pp. 116-117].

For what it's worth, the value of the effective grating space of a crystal  $d$  is calculated using Bragg's equation ( $\lambda = 2 \cdot d \cdot \theta$ ) from the observed deflection  $\theta$  of x-ray lines in the rule-grating method. The true grating space  $d'$  is obtained after correcting for refraction. Knowing the value of  $d'$ , we can calculate  $N$  from the equation:

$$N = M / [2 \cdot \rho \cdot \phi d']$$

where  $M$  is the molecular weight of the crystal,  $\rho$  is its density, and  $\phi$  is its geometrical constant. The value of  $e$  can then be derived from the Faraday constant. In a 1941 revaluation of the physical constants, Birge found  $N$  as  $(6.0228 \pm 0.0011) \cdot 10^{23} \text{ mole}^{-1}$  and  $e$  as  $(4.8025 \pm 0.0010) \cdot 10^{-10}$  esu based on the analysis of calcite at 20°C [Birge, pp. 117-119].

<sup>44</sup> See pp. 213-227 of Salmon's *Scientific Explanation and the Causal Structure of the World* for his argument for molecular reality based on the common cause principle.

1.  $P(A \& B/C) = P(A/C) \cdot P(B/C)$
2.  $P(A \& B/\neg C) = P(A/\neg C) \cdot P(B/\neg C)$
3.  $P(A/C) > P(A/\neg C)$
4.  $P(B/C) > P(B/\neg C)$

Conditions 1-4 entail that  $P(A \& B) > P(A) \cdot P(B)$ . To apply Reichenbach's notation, Salmon confined himself to two methods – alpha radiation and the Brownian movement. Other methods can be substituted for these two and the notation can also be generalized to more than two methods. In any case, Salmon says that conditions 1-4 hold for convergent determinations of  $N$  from the two methods A and B of alpha radiation and the Brownian movement under condition C of accurate measurements of directly measured parameters *and* the fact of molecular reality.

Peter Achinstein has rightly pointed out that Salmon's common cause argument does not necessitate discreteness.<sup>45</sup> While the appeal to Reichenbach's notation supports a common causal antecedent to the various determinations of  $N$ , the move from common cause to cause as discrete molecules is not obvious. Convergence supports that there is a common cause to the various phenomena, but it is not obvious that this common cause is the discreteness of matter.

### *Making sense of the converging range*

It is desirable that measurement results of a convergent value be amenable to greater precision. The greater the precision, the greater our confidence that variables affecting the phenomenon have been controlled for. Increasing precision then suggests

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<sup>45</sup> See Section 4 [A **Common-Cause Interpretation**] of Achinstein's essay *Evidence for Molecules: Jean Perrin and Molecular Reality* for his criticism of Salmon's argument. He says of Salmon's argument, "It is unproductive because a common-cause argument does not by itself make probable the existence of molecules" [Achinstein, p. 251].

that the quantity measured, which is typically a constant, is implicated in a true relationship. Huygens' convergent measurement of surface gravity was precise from the beginning, whereas Thomson's  $e/m$  measurement gained precision over six to ten years. As of 1913, the range from  $60 \cdot 10^{22}$  to  $75 \cdot 10^{22}$  for  $N$  had not achieved similar precision, and it was not clear whether  $N$  was amenable to greater precision.

The above range of values for  $N$  was not useless to the discreteness claim or the molecular hypothesis in general. It is just that  $N$  had not been decisively established as having a definite value, much less that value being an integer. Different people – Perrin and his contemporaries in 1913 and Bas van Fraassen today – saw the range as legitimizing different conclusions. Perrin saw it legitimizing the molecular origin of the Brownian movement. His vertical distribution results gave  $N$  values between  $65 \cdot 10^{22}$  and  $72 \cdot 10^{22}$ ; Perrin considered this in agreement with  $62 \cdot 10^{22}$  from the kinetic theory. He saw this as *decisive agreement* that left no doubt as to the origin of the Brownian movement:

It must be remembered that before these experiments were carried out we should certainly not have been in a position to deny that the fall in concentration through the minute height of a few microns would be negligible, in which case an infinitely small value for  $N$  would be indicated, or, on the other hand, to assert that all the grains do not ultimately collect in the immediate vicinity of the bottom, which would indicate an infinitely large value for  $N$ . It cannot be supposed that, out of the enormous number of values *a priori* possible, values so near to the predicted number<sup>46</sup> have been obtained by chance for every emulsion and under the most varied experimental conditions [Perrin 1913 b, Para. 65].

As it stands, this assertion amounts to saying that the derivation of the vertical

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<sup>46</sup> The number predicted on the kinetic theory.

distribution law supposes molecular reality, and the value of  $N$  from it agrees with  $N$  from the kinetic theory, which also supposes molecular reality. The agreement between Brownian movement experiments and the kinetic theory though is deeper than just that bare assertion. It extends to quantitative and qualitative features in granules compared to the kinetic theory. This will be the subject of Chapter IV on evidence for discreteness in the Brownian movement.

In pointing out the values *a priori* possible for  $N$  between zero and infinity, Perrin hints at the verification of the kinetic theory based on results from the Brownian movement. Bas van Fraassen agrees that the value of  $N$  between  $65 \cdot 10^{22}$  and  $72 \cdot 10^{22}$  legitimizes the kinetic theory, but this does not amount to the discreteness claim for him. He sees Perrin's determination of Avogadro's number as an enterprise in empirically grounding that constant within kinetic theory. Brownian movement directly measures  $N$  within the theoretical construct of the kinetic theory. According to Bas van Fraassen, this legitimizes the empirical application of the kinetic theory, but not the presuppositions of the kinetic theory about ontology.

Despite disagreement on the ultimate conclusions from Perrin's 1913 values for  $N$ , it seems that philosophers and scientists agree that convergence legitimized the application of the kinetic theory. Bas van Fraassen is willing to grant success based on convergence, but questions the step from success to belief in molecules [van Fraassen, p. 8]. He only compares the results from the vertical distribution of granules to results from the kinetic theory, and superficially at that, but there were 11 other determinations of  $N$  available to Perrin. In what follows, I will look at these determinations and the implications for their theoretical assumptions legitimized by convergence.

## Theory-Mediated Verifications of Discreteness

### *Discreteness of the elementary charge*

By 1913, direct measurements of small charges had revealed that such charges always come in integral multiples of the same quantity. The salient measurement is from Millikan's work on ionized oil-drops falling under the influence of an electric field. Before Millikan's work, the charge on ionized gaseous clouds had been measured to infer the charge  $e'$  on individual ions. Charged clouds obtained by the expansion of air would divide into two or even three clouds sinking at different rates under the influence of an electric field. Inferred values of  $e'$  from each cloud were proportionally as 1, 2, and 3 to each other [Perrin 1913 b, Para. 99]. The value of  $e'$  from the least charged cloud varied between  $2.7 \cdot 10^{-10}$  and  $4.4 \cdot 10^{-10}$  esu. Perrin duly noted for these results, "the want of precision is thus still great".

Inference to the elementary charge  $e$  from the study of clouds of ionized gas made the simplifying assumption that all the droplets in the cloud are identical. Inference to the elementary charge also did not account for frictional effects from the interaction of charged clouds with the sides of the containing vessel. The study of individual charged oil-drops overcame these problems. Reminiscing on the import of this innovation, Millikan said:

It now became possible to determine whether electricity in gases and solutions is actually built up out of electrical atoms, each of which has exactly the same value, or whether the electron which had first made its appearance in Faraday's experiments on solutions and then in Townsend's and Thomson's experiments on gases is after all only a *statistical mean* of charges which are themselves greatly divergent. The latter view has been strongly urged up to and even after the appearance of the work [on clouds of ionized gas] which is now under consideration [Millikan 1917, p. 56].



Millikan isolated droplets by passing them through a pinhole and followed individual droplets using an eyepiece. The droplet fell with a constant velocity  $v$  and under the influence of an electric field of magnitude  $E$ , rose with a constant velocity  $v'$ . The field  $E$  was used to balance the force due to gravity on the droplet to allow observation for several hours. Over several observations, sometimes the droplet velocity suddenly changed in a discontinuous manner from  $v'$  to  $v_1'$  due to a change in the charge from  $e'$  to  $e_1'$ . This variation became more frequent when the gas in which the droplet was moving was radiated while the oil-drop, made of a non-volatile substance, remained the same throughout the time of observation.

The ratio  $\frac{v+v'}{v+v_1'}$  gave the charge ratio  $\frac{e'}{e_1'}$ , and the comparison of  $v'$  to  $v_1'$  to  $v_2'$

and so on of successive velocities for a certain oil-drop showed that ratios of the charges as follows:<sup>47</sup>

2.00, 4.01, 3.01, 2.00, 1.00, 1.99, 2.98, 1.00

These charges are as whole number to one another with variation within one percent. For another drop, Millikan got the following values for successive charges with variation on the order of 1 in 300:

5, 6, 7, 8, 7, 6, 5, 4, 5, 6, 5, 4, 6, 5, 4

Systematic errors on the absolute value of the charges notwithstanding, these data proved that charge comes in multiples of a discrete unit. Comparison of Faraday's constant with the elementary charge then gives the number of elementary charges liberated in the electrolysis of one mole of a monovalent ionic compound, i.e. it gives Avogadro's number. It is significant that the parameter to derive  $N$  was measured directly and was

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<sup>47</sup> The data is as cited in Perrin's discussion on the *Atom of Electricity* [Perrin 1913 b, Para. 100].

discrete. Avogadro's number is an integer, albeit a very large one, to the extent that the Faraday constant is a unit of charge composed of discrete multiples of an elementary charge. Such an approach has the virtue of deriving  $N$  from discreteness in the direct parameter measured in addition to explaining the phenomenon of electrolysis on the theoretical assumption of discreteness. Convergence of  $N$  from measurement of  $e$  with other phenomena is equally important for the overall argument for discreteness, but it takes on added significance by being derived from a discrete parameter.

As for deriving a value for  $N$ , there were doubts on inferring the absolute value of the elementary charge from velocity measurements. Perrin wrote in *Les Atomes*, "The precise value of this elementary charge, which we now know to exist, has yet to be determined" [Perrin 1913 b, Para. 101]. The mass  $m$  of droplets had to be determined to calculate  $e$  from the ratio  $e/m$ . Stokes' law, applicable in liquids, did not work in gases where droplet radius is comparable to the mean free path of molecules.<sup>48</sup> Millikan corrected Stokes' law for gases to find  $e$  between  $4.86 \cdot 10^{-10}$  and  $4.92 \cdot 10^{-10}$  esu. A mean of  $4.89 \cdot 10^{-10}$  esu gave the value of  $N$  as  $59 \cdot 10^{22}$ . This is the value Perrin attributes to Millikan in *Les Atomes*. At that time, however, Millikan had actually found an improved value of  $4.774 \cdot 10^{-10}$  esu for  $e$  that he preferred<sup>49</sup> and that Perrin referenced while

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<sup>48</sup> The frictional effect reduces when the mean free path of molecules is comparable to the droplet radius and the uncorrected Stokes' law where  $mg = 6\pi a \xi v$  does not account for this. On extension of the simple law, the friction is independent of the pressure and this is clearly not the case when we realize that with increasing mean free path of molecules, the gas becomes rarified and the frictional effect decreases [Perrin, Para. 101].

<sup>49</sup> See "On the Elementary Electrical Charge and the Avogadro Constant" in *The Physical Review* [Vol. II, Series II] 1913, where Millikan undertakes a systematic redetermination of factors entering the Stokes' law with the view of "introducing certain improvements into the oil-drop method of determining  $e$  and  $N$ ".

reprimanding Millikan's probable error assignments.<sup>50</sup> So, Perrin knew about this more recent value – with  $N$  derived as  $6.06 \cdot 10^{23}$  from it – and it is not clear why he still attributed the outdated value to Millikan in *Les Atomes*.

Perrin ends the discussion of deriving  $N$  from  $e$  by noting repeat experiments on Millikan's work by Jules Roux working under Perrin. The presentation is quite brief and not very clear, but the idea is that Roux measured the rate of fall of spherules of super-cooled, pulverized sulfur in air and in a liquid, where Stokes' law applies. The value of  $e$  so derived lay between  $4.0 \cdot 10^{-10}$  and  $4.4 \cdot 10^{-10}$  with the mean of  $4.2 \cdot 10^{-10}$  giving  $N$  as  $69 \cdot 10^{10}$  within five percent. Perrin did not cite other sources confirming these results.

Millikan right away responded to Roux's work by noting in his 1913 revaluation of  $e$  and  $N$  that the correcting parameter  $A$  for Stokes' law used by Roux was twice too large – about 1.63 instead of Millikan's 0.874. Roux would have discovered this by observing spherules<sup>51</sup> of different sizes or at different pressures, but he assumed a “purely theoretical value” [Millikan 1913, p. 110]. Millikan also questioned the sphericity and density measurement of solid spherules compared to oil-drops, and ended by citing alternate studies on solid spherules, using the correct value for  $A$ , from the Ryerson Laboratory under A.A. Michelson that “yield[ed] results very close to those obtained with oil drops”.

It is possible that, while writing *Les Atomes*, Perrin did not know of Millikan's critique of Roux's determination of  $e$  or the determination of  $e$  at the Ryerson Laboratory. It is also possible that he overlooked them because the value of  $N$  based on Roux's work

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<sup>50</sup> In reference to Millikan's probable error assignment of 1 in 2,000 for the mean value  $4.89 \cdot 10^{-10}$ , Perrin remarks that such a high degree of precision is very doubtful, especially since Millikan in a later publication himself raised the value he proposed for  $N$  by two percent. The value of  $e$  as  $4.774 \cdot 10^{-10}$  yields such an increase.

<sup>51</sup> Millikan calls them spheres, but I am sticking with Perrin's usage of spherules to be consistent.

$-69 \cdot 10^{22}$  – converges very well with his determination based on the vertical distribution of granules  $-68 \cdot 10^{22}$ . As discussed above, the range of  $N$  was between  $60 \cdot 10^{22}$  to  $75 \cdot 10^{22}$  with no obvious way of reconciliation. If Perrin had to pick between his own experimental work and Millikan's, his past achievements justified his picking his own.

This episode is perhaps evidence that there was no clear idea on what the range of values for  $N$  was converging to. Whether there was even a value to converge to was an open question, but experimental work, especially on the determination of  $e$ , was being carefully scrutinized for systematic errors or otherwise to answer this question. In such an environment, clear verification of discreteness in the elementary charge gave reason to be optimistic about a well-defined value of  $N$  at some point in the future. Verification of this sort was not confined to electrochemistry and was also seen in studies on radioactivity, especially in the measurement of alpha rays.

### *Radioactivity: Counting Helium atoms*

In 1896, Henri Becquerel discovered radioactivity quite by accident while studying a phosphorescent uranium salt. He found uranium rays of a feeble yet constant intensity, which depended only on the mass of uranium present. They remained constant in light or in darkness, at high or at low temperatures, and were unlike substances that emitted ionizing rays in a temporary manner as the result, for instance, of a chemical reaction [Perrin 1913 b, Para. 105]. The phenomenon of such emission was given the name of Radioactivity by Marie Curie. She obtained pure salts of a new element, radium, from solution and crystallization of uranium and thorium samples, which, owing to trace amounts of radium in them, were 8 times more active than a pure uranium or thorium sample would indicate. Radium was at least a million times more radioactive than

uranium. The study of various radioactive preparations in Crookes' tubes led to the discovery of three types of radiation:  $\alpha$  rays,  $\beta$  rays, and  $\gamma$  rays.

Alpha rays played a central role in all four determination of  $N$  from experiments on radioactivity. The alpha rays from radium are complex and consist of particles projected with very different velocities. They are unequally deflected in electric and magnetic fields. By 1906, Rutherford had obtained a homogenous source of alpha rays from an active wire exposed to radium emanation [Rutherford 1906, p. 122]. He obtained a value between  $5.0 \cdot 10^3$  and  $5.2 \cdot 10^3$  on the electromagnetic system of units for the charge to mass ratio of homogenous alpha rays. By 1908, he had a more precise value of  $5.07 \cdot 10^3$ . Furthermore, he found the charge on individual alpha particles by comparing the charge collected to the number of alpha particles expelled in unit time. He obtained a value of  $9.3 \cdot 10^{-10}$  esu [Rutherford and Geiger 1908 b, p. 168]. The alpha particle was either a hydrogen molecule with an elementary charge or a helium atom with two elementary charges.

William Ramsay and Frederick Soddy had observed helium production in radium emanation as early as 1903. Isolation studies of the other component of radium emanation had also revealed its density, molar weight, line spectrum, and that it was chemically inert<sup>52</sup> – in short, that it was a definite chemical element. Ramsay proposed to call it Niton, known as Radon today. The atomic weight of radium was very nearly the sum of the atomic weights of niton and helium, further evidence for the *transmutation* of radium into helium and niton [Perrin 1913 b, Para. 108]. In 1909, Rutherford collected alpha

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<sup>52</sup> Ramsay and Soddy found that radium emanation could withstand the action of reagents – “[it] could be passed without alteration over platinum and palladium black, chromate of lead, zinc dust, and magnesium powder, all at a red-heat” – hitherto unobserved except in the inert gases, like argon [Ramsay and Soddy, p. 205].

particles in a vessel and spectroscopically proved that the collected material was helium. From this and from data on the electric and magnetic deflection of alpha rays, Rutherford concluded, “The experiments give a decisive proof that the  $\alpha$  particle after losing its charge is an atom of helium” [Rutherford and Royds 1909, p. 286]. Experimental work thus uniquely identified alpha particles as discrete helium ions. The evidence for discreteness was in convergent counting techniques of alpha particles.

Sir William Crookes and also Elster and Geitel discovered in 1903 that if a screen coated with small crystals of phosphorescent zinc sulphide is exposed to alpha rays, a brilliant luminosity is observed. On viewing the surface of the screen with a magnifying glass, the light from the screen is revealed as a number of scintillating points of light scattered over the surface and of short duration. Regener was the first to count the number of scintillations to determine the number of alpha rays incident on the screen. Rutherford said of this method:

This beautiful experiment brings vividly before the observer the idea that the radium is shooting out a stream of projectiles each of which causes a flash of light on striking the screen” [Rutherford et. al 1930, Para. 12b].

Rutherford and Geiger devised a more precise method of counting alpha rays by filtering them through a mica diaphragm into a rarefied gas between two electrified plates. Each alpha projectile produces a trail of ions, which move toward either pole based on their sign. When the gas is sufficiently rarified and the electric potential is sufficiently high, the ionized molecules acquire sufficient velocity to split up molecules that they meet. The trail of ions and the subsequent molecules ionized lead to a discharge large enough to register as noticeable deflections of an electrometer needle connected to

one of the electrifying plates.<sup>53</sup> Based on this method, Rutherford found that a gram of radium emits  $34 \cdot 10^9$  alpha projectiles per second, and his results converged with Regener's determinations.

We saw above that Rutherford, working with Geiger, obtained a value of  $9.3 \cdot 10^{-10}$  esu for the charge on individual alpha particles. They counted the number of particles by convergent methods of a Geiger counter and the scintillation technique. Using a strong magnetic field, to remove beta particles, they isolated alpha particles into a Faraday cylinder and found the charge  $Q$  on just the alpha particles. The quotient of the charge to the number of particles thus gave  $9.3 \cdot 10^{-10}$  esu for the charge on each alpha particle. Previous determinations of  $e/m$  of alpha particles established they were helium atoms carrying two elementary charges each. This gave  $4.65 \cdot 10^{-10}$  esu for the elementary charge and  $N$  as  $62 \cdot 10^{22}$  within ten percent. In addition to this indirect method of determining  $N$  from the elementary charge based on alpha particle emissions, the following two methods equated alpha particles with (1) the quantity of helium produced and (2) the quantity of radium lost.

The first of these equated the emission of each alpha particle with the production of a helium atom, as stated in equation [11] from Chapter II. Measurements by Sir James Dewar and subsequently by Boltwood and Rutherford indicated  $156 \text{ mm}^3$  of volume liberated annually per gram of radium, which corresponds to  $39 \text{ mm}^3$  of helium. The

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<sup>53</sup> Rutherford and Geiger commented that their method was based on the property discovered by Townsend, that an ion moving in a strong electric field in a gas at low pressure, produces a number of fresh ions by collision with the gas molecules. The alpha particles were directed towards a collecting vessel, where they were detected by a "sudden throw of the electrometer needle" [Rutherford and Geiger 1908 a, p. 2]. Based on the number of  $\alpha$  particles shot through the opening per minute from the number of throws, the total number fired out the radioactive material could be calculated from the known area of the opening of the testing vessel and its distance from the active matter.

number of alpha particles emitted per gram of radium per year corresponding to this volume is  $34 \cdot 10^9 \cdot 86,400 \cdot 365$ . This multiplied by  $22,400 \text{ cm}^3$  – the volume occupied by the gram molecule of a gas – gives  $62 \cdot 10^{22}$  helium atoms per mole, i.e. Avogadro's number. The other method compared alpha rays emitted per gram of radium per second with the fraction of radium lost per second. This led to equation [12] from the previous chapter. The molar mass of radium was known as 226.5 grams, and the fraction of radium lost in the first second was known by its half-life.  $N$  calculated this way was:

$$226.5 \cdot 34 \cdot 10^9 = N \cdot 1.09 \cdot 10^{-11}$$

$$N = 71 \cdot 10^{22}$$

If alpha rays consist of discrete alpha particles, their relationship to Avogadro's number implies that  $N$  is an integer. To the extent that discrete scintillations on a phosphorescent screen or the discrete jerks of an electrometer needle are alpha particles, their relation to helium produced or radium lost implies discreteness in the quantity of helium produced or radium lost. Rutherford had convinced everyone by 1909 of the identity of alpha rays as helium ions, and  $e/m$  determinations of alpha rays were equal to that of a helium atom with two elementary charges. The  $e/m$  could have also been a hydrogen molecule with an elementary charge, but experimental work by Rutherford and Royds precluded this by 1909. The study of alpha rays thus implied that  $N$  is an integer, even if a very large one and one that we may never know the exact value of.

## **Revisiting the 1913 Converging Range**

### *Discreteness in indirect measurements of $N$*

Rutherford had one last method of determining  $N$  from the energy radiated by radium. He assumed that the kinetic energy of alpha particles is equivalent to the heat continually liberated by radium, which had been measured as 130 calories per gram per



hour. This led to equation [13] from the previous chapter, from which Rutherford found  $N$  as  $60 \cdot 10^{22}$ . Although the determination of initial velocities in this method was not as direct as the methods for counting alpha rays, it is meaningful that  $N$  determined this way converged with  $N$  from the direct determinations of discrete alpha particles.

The emission of heat is an apparently continuous phenomenon and was the basis of the phenomenological interpretation of thermodynamics. The value of  $N$  based on heat liberated by Radium is not obviously an integer. That would require a statistical interpretation of the second law of thermodynamics, something that the proponents of the Energetics doctrine resisted; there was indeed no reason to accept the statistical interpretation based solely on the fact that a value for  $N$  was found. Support for the statistical interpretation had to be found elsewhere, and this is where discreteness in the details of the experiments became relevant. Although heat emission is an apparently continuous phenomenon, it is connected to the emission of discrete alpha particles in radioactivity. The convergence of  $N$  from methods that have directly measured discrete parameters with methods that are apparently continuous, but can be given a statistical interpretation, supports the statistical interpretation of the second law.

The support for discontinuity underlying apparently continuous heat flow, from convergence of  $N$ , extends to other apparently continuous phenomena.  $N$  is discrete to the extent that it is related to discrete elementary charges in the Faraday constant or to discrete alpha particles in the amount of helium produced, radium lost, or heat emitted in radioactivity. When this constant shows up in the lateral diffusion of light through an apparently homogeneous sample of argon or apparently homogeneous air, the evidence for discreteness from studies in electrochemistry and radioactivity supports fluctuations

of discrete units underlying the diffusion phenomena. Fluctuation of molecules was the theoretical assumption underlying Smoluchowski's derivations, and convergence of  $N$  legitimized the *application* of this assumption to derive law-like relationships. Convergence of  $N$  with discrete phenomena legitimized the *theoretical assumptions*, i.e. it legitimized and gave grounds for the ontology of Smoluchowski's presuppositions.

### *Setting the stage for the Brownian movement*

At face value, the 1913 range of  $N$  from  $60 \cdot 10^{22}$  to  $75 \cdot 10^{22}$  did not obviously establish that  $N$  is an integer and that atoms and molecules exist. This worry is addressed to some extent by close examination of phenomena in which discreteness was directly measured. Discreteness in measurements of the elementary charge and alpha particles gave grounds for seeking systematic errors in measurements of  $N$  in various phenomena – 13 equations to be exact – to reconcile the outstanding range. In hindsight, we know that Perrin's Brownian movement measurements gave too high a value of  $N$  because of the nature of the method itself.<sup>54</sup> Even in 1913, Millikan had shown, in his revaluation of the value of the elementary charge, that the search for systematic errors can give better values for a constant. Experimental work on determinations of the elementary charge, the emission of alpha particles, half-life values, and the distribution, displacement, and rotation of granules was still going on in 1913 to seek out systematic errors. Based on the measurements of  $N$  from electrochemistry and radioactivity, there was good reason to suppose that a well-defined value of  $N$  would come out of this effort.

Although studies in electrochemistry and radioactivity suggested that a well-

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<sup>54</sup> Nye points out, "Throughout his work on Brownian movement, Perrin's values of  $N$  were consistently too high, though the imprecision was due to the nature of the methods themselves, rather than to any failure on his part" [Nye, Footnote 104 to Chapter III].

Thus far, I have been unable to find out what about the Brownian movement consistently gave too high a value of  $N$ .

defined value of  $N$  was on the horizon, the Brownian movement was the singular phenomena that convinced scientists at large of discreteness. The Brownian movement consisted of discrete granules, like charges on Millikan's oil drops or alpha particles from Rutherford's Geiger counter, but these were also visibly discrete. Furthermore, the quantitative study of the Brownian movement initiated by Perrin, and supported by Einstein and Smoluchowski's theoretical work, was an extension of the gas laws. If experimental work on the Brownian movement agreed with the theoretical assumptions of the gas laws and the kinetic theory, there would be strong grounds to suppose that granules simulate molecular motion by proxy.

## IV: ‘Seeing’ Molecules in the Brownian Movement

### **The Range of Data on the Brownian Movement**

In the last chapter we saw discreteness in measurement of the elementary charge and alpha particles. They indirectly support that  $N$  is an integer or, in other words, that matter is discrete, and could thus be considered evidence for the discreteness of matter by proxy. Observations of the Brownian movement, in contrast, were more along the lines of direct evidence for the discreteness of matter. The value of  $N$  derived in Brownian movement experiments from discrete granules was in agreement with the kinetic theory; moreover, Perrin showed that the gas laws rigorously applied to emulsions. This first convinced many of Perrin’s contemporaries of the discreteness of matter. In the preface of the 4<sup>th</sup> edition of his *Grundriss der allgemeinen Chemie*, written in 1909, Ostwald famously responded:

*I have convinced myself that we have recently come into possession of experimental proof of the discrete or grainy nature of matter, for which the atomic hypothesis had vainly sought for centuries, even millennia.* The isolation and counting of gas ions on the one hand – which the exhaustive and excellent work of J.J. Thomson has crowned with complete success – and the agreement of Brownian movement with the predictions of the kinetic hypothesis on the other hand, which has been shown by a series of researchers, most completely by J. Perrin – this evidence now justifies even the most cautious scientist in speaking of the experimental proof of the atomistic nature of space-filling matter. What has up to now been called the atomistic hypothesis is thereby raised to the level of a well-founded theory... [Quotation from Brush, p. 35].

It is noteworthy that Ostwald singled out the isolation and counting of gas ions, which amounts to verification of discreteness in the measurement of the elementary charge, as

important for the discreteness claim. The measurement of such ions was the subject of the last chapter. We now turn our attention to the Brownian movement.

By 1908 Perrin had conducted three series of experiments, with grains of very different sizes, on the vertical distribution of granules leading substantially to the same value of  $N$ . By December of that year, he had data on 13,000 grains from 16,000 readings [Perrin 1908 b, p. 595].<sup>55</sup> Upon realizing the connection between his 1908 experiments and Einstein's theoretical work on the Brownian movement from 1905, Perrin put the theory to test using methods of preparation, observation, and measurement that he had perfected by now. Starting this work in 1909, Perrin expected negative results based on experimental work by Svedberg and especially Henri that contradicted Einstein's equations [Nye, p. 128]. Svedberg had found the mean square of displacement ( $x^2$ ) proportional to  $t$  but 6 to 7 times greater than Einstein's calculation. Henri had found the same relation to be 4 times greater [Brush, p. 33]. Henri questioned Stokes' law for small particles, but Perrin eliminated this worry by 1908 with his convergent measurements of granule radii. Henri's evaluations of granule size had been inaccurate, and Cotton has conjectured that a large quantity of light in Henri's cinematographic studies had influenced the mean temperature of emulsions as well [Nye, p.126]. In any case, Chaudesaigues working under Perrin found  $N$  as  $64 \cdot 10^{22}$  and concluded that Einstein's formula was exact. By 1913, Perrin had carried out seven series of experiments establishing the validity of Einstein's theoretical derivations and ten series confirming his vertical distribution law.

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<sup>55</sup> In the December 1908 publication, *Grandeur des molécules et charge de l'électron*, Perrin also discussed convergent measurements of  $N$  for the first time.

## Stability in the Brownian Movement

Molecular magnitudes derived from Brownian granules coincided with other methods; moreover, Perrin found a stable value over a wide range. In one series of measurements after another, he varied conditions for the viscosity, temperature, volume, and density of granules. As mentioned above, by the time *Les Atomes* was published Perrin had varied the viscosity in ratios of 1 to 250, the temperature from 1.26 to 1 on the Kelvin scale, the volume from 1 to 50, and the density from 1 to 5. In one series of experiments pursued with Niels Bjerrum, Perrin studied an emulsion of gamboge in 88% glycerin, which is 115 times more viscous than pure water, with hopes of approaching the rigidity of solids [Nye, p. 130]. Perrin found converging molecular magnitudes from one series to another and thought he had found a method, “qui me semble *directe et susceptible d’une précision illimitée*” [Perrin 1908 b, p. 595].

The constancy of  $N$  over a wide range of parameters made a strong case that this constant is implicated in a true relationship for the distribution, mean displacement, mean rotation, and diffusion of Brownian granules. As the parameters were varied, granular activity varied to give consistently the same value of  $N$ . The range of parameters in Perrin’s experiments was truly impressive; more impressive was the virtual constancy of  $N$  across all measurements. The method of viscosity measurements to find  $N$  exhibited a somewhat comparable range, but did not have an equally stable value of  $N$ . The 1899 standard text on the *Kinetic Theory of Gases* by Oskar Meyer boasted an impressive range of fourteen gases to find  $N$ ,<sup>56</sup> but the values varied from  $1.7 \cdot 10^{22}$  to  $8.1 \cdot 10^{22}$  with a

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<sup>56</sup> Meyer and others at the time looked at Loschmidt’s number, but the mole was a known standard. Conversion from Loschmidt’s to Avogadro’s number easily follows from a conversion of the amount of an ideal gas in a cubic centimeter to the amount in a mole, which is  $22,400 \text{ cm}^3$  at STP.

mean of  $4.2 \cdot 10^{22}$ . Meyer cautioned that the values based on this method were too small,<sup>57</sup> but  $N$  even from his preferred method of the dielectric capacity of gases varied from  $120 \cdot 10^{22}$  to  $370 \cdot 10^{22}$  with a mean around  $220 \cdot 10^{22}$ . Meyer full well recognized the problem and was content with admitting in 1899 that, “We must rejoice and, at least provisionally, be content that we have found values which differ only so little from each other that they, in all cases, are of the same order of magnitude [based on the separate methods]” [Meyer, Para. 118].

The combined range of  $N$  from  $4.2 \cdot 10^{22}$  to  $370 \cdot 10^{22}$  based on measurements of viscosity and dielectric constants from 1899 threatens to suggest that  $N$  is an artifact of the measurement process. The hypothetical nature of the determinations did not alleviate this worry. Corrections to obtained values seemed a matter of taste and rather ad hoc at times – for instance, the correction that molecules are not perfect spheres, as the determination based on viscosity supposes, makes the actual value of  $N$  more or less greater than the calculated value. A defender of the Energetics movement could have said at the time that the constancy of  $N$  is merely wishful thinking and the numbers calculated from viscosities and dielectric constants are mere contingencies – they could be measures of temporary vortices or internal microscopic vibrations within a continuous medium rather than discrete atoms and molecules.

To the extent that determinations of  $N$  are tightly bound, the worry that  $N$  is an artifact of the measurement process is mitigated. Perrin’s 1908 range for  $N$  from  $65 \cdot 10^{22}$  to  $72 \cdot 10^{22}$ , based on extensive series of measurements over a wide range of experimental

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<sup>57</sup> Implied by Meyer in his comment on the calculation of the molecular diameter ( $s$ ) from viscosity measurements: “We may not, therefore, take the values calculated for  $s$  as giving the true size of the molecules, but may see in them only a superior limit which the size of the molecules does not attain” [Meyer, Para. 116].

parameters, goes a long way in tightening the 1899 range for  $N$  from  $4.2 \cdot 10^{22}$  to  $370 \cdot 10^{22}$ . At the same time, the closer range does not completely put to rest the objection that  $N$  may not be an integer. Achinstein makes this point while criticizing Clark Glymour's breakdown of Perrin's experiments.<sup>58</sup> Glymour appeals to a "bootstrapping" method by which Perrin's equations relate  $N$  to measurable quantities to compute a value for  $N$ .<sup>59</sup> Using another set of measured quantities, Perrin instantiates his equations and his value for  $N$ . While that may be, Achinstein has noted that the "bootstrapping" method allows "confirmation of equations containing completely undefined or meaningless terms".<sup>60</sup> More to the point,  $N$  need not be given a molecular interpretation on this account; it is instantiated as a constant of proportionality, but that does not make it an integer.

On account of the stable measurement of  $N$ , it is not clear exactly at what point the range is close enough to legitimize viewing  $N$  as an integer in the gas laws or the laws of emulsions. Irrefutable evidence in this respect would perhaps be a stable determination of  $N$  to all its 24 digits and some zeroes in the decimal place. We need not dwell on how many zeroes are needed in the decimal place, however, for this method of confirmation is quite impractical. Even though Perrin thought his method was capable of unlimited precision, this is an unrealistic standard to meet.

In another respect, discreteness was evident in the direct phenomenon being studied to the extent that Perrin was directly counting discrete particles in equilibrium.

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<sup>58</sup> See section 6 [**Bootstrapping**] of Achinstein's essay, *Evidence for Molecules: Jean Perrin and Molecular Reality* for his criticism of Glymour's account [Achinstein, pp. 252-253].

<sup>59</sup> While discussing the method of instantiating undetermined constants in an equation, Glymour remarks, "Some of Jean Perrin's tests of equations of the kinetic theory are exactly of the kind illustrated. Perrin had, for instance, to use one of the equations to be tested to determine a value for a constant (Avogadro's number) it contained" [Glymour, Footnote 12 on p. 409].

<sup>60</sup> Achinstein provides a general criticism of the "bootstrapping" method in Chapter 11 of his book, *The Nature of Explanation*.



The Brownian movement was an extension of the gas laws, and discrete granules of gamboge and mastic were the objects of this extension. A verification of the experimental laws of the Brownian movement derived by Perrin, Einstein, and Smoluchowski against the gas laws and the kinetic theory would empirically support a phenomenon in which the discreteness of matter is directly evident.

## **The Singular Phenomenon of the Brownian Movement**

### *General View on the Brownian Movement Experiments*

In *Molecular Reality*, Nye proposes the significance of Perrin's work on granules as being the first direct determination of molecular magnitudes. There were indirect determinations based on gas viscosities and relative values had been found in Thomson's  $e/m$  determinations. The phenomenon of Brownian movement presented the first opportunity of direct and absolute measurement of visible particles. Nye concludes, "if values derived from granules coincided with figures calculated from indirect and relative methods, the foundations of the kinetic theory would rest assured, as would the absolute truth of molecular reality" [Nye, p. 91].

Philosophers like Peter Achinstein and Stathis Psillos have also noted the significance of Brownian movement experiments over other experiments.<sup>61</sup> They agree with Nye that Brownian movement experiments were direct in a significant way, but have not discussed in detail why exactly that was so. Achinstein at least comments that

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<sup>61</sup> For Achinstein's argument, see his essay, *Evidence for Molecules: Jean Perrin and Molecular Reality* in *Book of Evidence*. For Psillos' argument, see *Moving Molecules Above the Scientific Horizon: on Perrin's Case for Realism* in *Journal for General Philosophy of Science*, vol. 42: pp 339-363. Also see Psillos' critique of Achinstein in *Making Contact with Molecules: on Perrin and Achinstein* in *Philosophy of Science Matters: the Philosophy of Peter Achinstein* by Gregory J. Morgan. Here Psillos argues that his Bayesian notation is superior to Achinstein's because he explicitly points out the importance of Perrin's experiments and their agreement with the atomic hypothesis. At the same time, he fails to discuss the reasons exactly why Perrin's experiments are strong support for the atomic hypothesis.

Brownian movement experiments achieved an access that had not been achieved before. There had been indirect evidence for molecules from chemistry based on the regularities of chemical composition and proportions, from physics in the kinetic theory of gases, but the effect of molecules was evident in the Brownian movement. Achinstein says:

For Perrin, Brownian movement was for molecules what cathode rays were for electrons.

Both phenomena provided a relatively direct link between the postulated entities and their observable effects [Achinstein, p. 291].

While that may be, this reasoning does not capture that the irregular motion of granules themselves is an extension of the gas laws and an instance of molecular movement. Furthermore, the instance of cathode rays in itself does not establish that electrons come in discrete units of charge as much as it establishes that cathode rays are streams of negatively charged particles. Similarly, the instance of Brownian movement in itself does not establish that matter around the granules is discrete as much as it establishes that matter around the granules is causing the movement, i.e. the Brownian movement is internal to the fluid. The inference to discrete atoms and molecules is dependent on theoretical connections of the Brownian movement to the gas laws and the measurement outcomes therein.

### *The Import: Connecting the Microcosm to the Macrocosm*

The connection of the elementary charge to molecules was based on electrolysis and the charge liberated during that, the Faraday constant. The connection of alpha particles to molecules was based on nuclear physics and the change in the internal structure of nuclei. The connection of granules in an emulsion to molecules was more direct, as they were an extension of molecular motion. This seems to be the important

idea, where the Brownian movement amounts to molecular motion. This was also Perrin's view, which he expressed in his 4<sup>th</sup> paper on the Brownian movement in 1908:

The law on the vertical distribution of granules in an emulsion is based on the extent to which molecules of the same mass would distribute under the gas laws [Perrin 1908 b, p. 595].<sup>62</sup>

Similar views are apparent in Perrin's publications from earlier that year. In his 1908 *L'origine du mouvement brownien*, Perrin followed the results on the vertical distribution of the heaviest of the granules with the comment that we can say these granules are molecules of an ideal gas with a molar mass of 300,000 grams. This was the kind of convergence that did not leave any doubt in Perrin's mind of the discreteness of matter and the rigorous application of the kinetic theory [Perrin 1908 a, p. 532].

The extension of molecular diffusion, distribution, displacement, and rotation in the Brownian movement is also what Poincaré found most important. Impressed by Perrin's experimental verification, Poincaré commented on the parallels between the kinetic theory of gases, the Brownian movement, and the electronic theory of metals:

The parallelism is perfect and can be pursued even to numerical coincidences... each of these three theories, if it were isolated, would seem to be merely an ingenious hypothesis, for which it would be possible to substitute other explanations nearly as plausible. But, as in each of the three cases a different explanation would be necessary, the coincidences which would have been observed could no longer be attributed to chance, which is inadmissible, whereas the three kinetic theories make these coincidences necessary [Poincaré 1913, p. 90].

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<sup>62</sup> The original French, "elle se fonde sur ce que des grains égaux se répartissent dans une émulsion étendue comme feraient des molécules de même masse obéissant aux lois des gaz parfaits" [Perrin 1908 b, p. 595].

The three kinetic theories were extensions of the same kinetic laws over different domains, which led Poincaré to conclude: “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 [Poincaré 1913, p. 89].

Although Perrin had a few ways of connecting the gas laws to emulsions, his clearest derivation is in *Les Atomes*.<sup>63</sup> He considered a thin cylindrical element of unit cross-sectional area. There are pressures  $p$  and  $p'$  at the bottom and top of the element respectively. Pressure  $p$  is greater than  $p'$ , just as air pressure at the bottom of a mountain is greater than at the top. The force of gravity  $g \cdot m_g$  balances the  $\Delta p$ .

$$p - p' = m_g \cdot g$$

The mass of the element is to its molar mass as its volume ( $1 \cdot h$ ) is to the volume occupied by a mole under the same mean pressure, so that:

$$p - p' = g \cdot \frac{M}{v} \cdot h$$

where  $M$  is the molar mass and  $v$  is the volume occupied by the molar mass. By the ideal gas law for a mole of gas,  $[p \cdot v = R \cdot T]$ ,  $v$  is as  $\frac{R \cdot T}{p}$ , which makes the change in pressure:

$$p - p' = \frac{M \cdot g \cdot h}{R \cdot T} \cdot p$$

$$\frac{p'}{p} = 1 - \frac{M \cdot g \cdot h}{R \cdot T}$$

where  $R$  is the gas constant and  $T$  is the absolute temperature. This is the law of atmospheres, which had been verified for atmospheric air, oxygen gas, and could be

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<sup>63</sup> From Para. 54 & 55 of *Les Atomes*. Einstein also derived an equivalent function,  $\Delta V = \frac{M \cdot g \cdot h}{R \cdot T}$ , in his 2<sup>nd</sup> 1905 paper on the Brownian movement.

extended to other gases based on relative molar masses. At this point in the derivation, Perrin cautioned, “The preceding arguments are clearly applicable to emulsions, *if they obey the gas laws*” [Perrin 1913 b, Para. 55].

Direct measurement of the mass of a molecule was not feasible, and thus only relative masses could be determined from the law of atmospheres. Absolute values could be obtained from the relation of Avogadro’s number to the molar mass, but Avogadro’s number was obtained indirectly, either from viscosity measurements or electrolysis studies. Perrin’s work on the Brownian movement changed this. While molecular masses could not be directly measured, Perrin could directly measure granular masses. In the law of atmospheres, he substituted  $N \cdot m$  for  $M$  where  $N$  is Avogadro’s number and  $m$  is the mass of one molecule. Change in pressure is proportional to change in density, and for molecules or granules, density is proportional to their number per unit volume. The law of atmospheres thus gives us the law for the vertical distribution of molecules *or* granules:

$$\frac{n'}{n} = 1 - \frac{N}{RT} m \cdot g \cdot h$$

Lastly, Perrin had to account for the effective weight of the granules, due to the up-thrust provided by the intergranular liquid:

$$\frac{n'}{n} = 1 - \frac{N}{RT} m \left( 1 - \frac{d}{D} \right) gh$$

Perrin then embarked on (1) the verification of this relationship and (2) its comparison with the kinetic theory. He had developed theory and experimental procedure to a point where the empirical world could decide whether granules in an emulsion distribute themselves as molecules of the same mass would.

### *Molecular Motion by Proxy: Experimental Verification*

The analogy between gas molecules and granules links the two phenomena; but we can see the granules and measure their mean distribution, displacement, rotational motion, and rate of diffusion. The extent to which this extension is empirically verified in the Brownian movement, the gas laws are empirically verified by proxy. This was Perrin's view behind comparing the osmotic pressure of an emulsion – where osmotic pressure =  $k \cdot n$ , and  $n$  is the concentration of granules – with the pressure in the same volume by the same number of molecules of an ideal gas – where pressure =  $n \cdot \frac{RT}{N}$ ,  $R$  is the gas constant,  $T$  is the absolute temperature, and  $N$  is Avogadro's number [Perrin 1908 a, p. 531].

In his 1908 *L'origine du mouvement brownien*, Perrin determined  $k$  as  $42.5 \cdot 10^{-15}$  from a first series of experiments giving  $N$  as  $57 \cdot 10^{22}$ . In two more series with granules 8 and 27 times heavier, he found  $k$  equal to  $40.4 \cdot 10^{-15}$  and  $44 \cdot 10^{-15}$  with corresponding values of  $N$  as  $60 \cdot 10^{22}$  and  $54 \cdot 10^{22}$  respectively. Perrin remarked that the granules in the last set are so big that their concentration falls to a quarter the initial value with an elevation of only 8 microns. This same rarefaction is achieved in air with an elevation of 12 km. As mentioned above, Perrin said that these are molecules of an ideal gas whose molar mass is about 300,000 grams. He is clearly pursuing the analogy of granules with gas molecules here, playing on the fact that the gas laws and magnitudes for invisible molecules extend to visible granules in an emulsion.

Recalling the search for an analogy between the microcosm of the gas laws and the macrocosm of granules in an emulsion, Perrin said this in his 1926 Nobel Prize acceptance speech:

It will be sufficient for us to find an experimentally accessible property for emulsions which would be logically equivalent to the gas laws.

I found such a property (1908) by extending to emulsions the fact that is qualitatively well known to you, that in a vertical column of a gas in equilibrium the density decreases as the altitude increases [Perrin 1926].

By 1913, he had verified this extension in ten series of experiments on the vertical distribution of granules and in seven series on Einstein's displacement formula.

The 1908 verifications by Perrin mostly dealt with the vertical distribution of granules, but soon afterwards he conducted experiments on the movement of granules – the mean square of their displacement and rotation. Similar to his vertical distribution studies, Perrin observed the displacement of granules over a wide range of experimental conditions. From mass ratios varying as 15,000 to 1 and viscosities varying as 125 to 1, he consistently got  $N$ , based on equation 1.6, around  $64 \cdot 10^{22}$ . Perrin's student, Chaudesaigues, also observed the distribution of granules to confirm Maxwell's law of the Gaussian distribution of displacements in granules.

Although the numerical convergence of  $N$  from experiments on the diffusion, distribution, displacement, and rotational motion of granules was important, Perrin accomplished even more in his Brownian movement studies. He confirmed qualitative as well as quantitative features of the kinetic theory in granules. He showed that the laws of emulsions are equivalent to the gas laws, i.e. the gas laws rigorously apply to granules. Perrin confirmed that there is agreement between the mean kinetic energy of the granules, measured directly, and the mean kinetic energy of molecules, derived from the kinetic theory. He found agreement between qualitative features like the equipartition of energy across degrees of freedom, the increase in particle agitation with temperature, and the

increase in measured velocity with diminishing periods of observation  $\tau$ .<sup>64</sup> In addition, Perrin confirmed the applicability of the law of probabilities in the distributions of the displacements of granules.

### **The Access achieved in the Brownian Movement**

Perrin's case for the discreteness of matter is instructive in showing that seeing molecules is not the only way to establish their existence. This is not to say that establishing the discreteness of matter amounts to imagining atoms and molecules as they are. If we remember Heisenberg's remark, that is in fact impossible. At the same time, it is possible to establish the discrete or particulate nature of matter without actually seeing the discrete particles. Psillos puts it well that, in Perrin's case, the real issue about the so-called theoretical entities is not their unobservability, but rather their *accessibility* [Psillos 2011 a, p. 185].

Observations of the Brownian movement, however, are not far from actually seeing molecules. If the extension of the gas laws to granules is legitimate, granules are just very large molecules – with a molar mass around 300,000 grams, as Perrin noted. Perrin verified the extension of the gas laws in emulsions over an impressive range of parameters, in many series of experiments. This promised to satisfy even Duhem's criterion of those rare times when a physical theory can make us “see with our own eyes the motions to which it attributes [certain] phenomena” [Duhem, p. 8]. Duhem mentions acoustic theories as rare examples that *explain* experimental laws by reference to motions

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<sup>64</sup> This is an outcome of Einstein's derivation of mean displacement, which implies that any direct attempt to measure the “instantaneous velocity” is contingent on the time period of observation and is meaningless for measuring the desired parameter. Of course, it also implies an infinite instantaneous velocity at short intervals, which Einstein duly noted. This is due to the idealization that events during time  $t$  are independent of the events in the time immediately preceding. The equation can be modified over short intervals to give physically reasonable results in the form of the “Ornstein-Uhlenbeck process” [Brush, pp. 23-24].



that we can see with our own eyes and feel with our own fingers. He is talking about waves on a string. The experimental laws of acoustics enunciate the fixed relations among abstract notions such as intensity, pitch, octave, timbre, etc., but theories of acoustics teach us that, “where our perceptions grasp only that appearance we call sound, there is in reality a very small and very rapid periodic motion; that intensity and pitch are only external aspects of the amplitude and frequency of this motion...” [Duhem, p. 8].

To suppose that intensity and pitch originate in the amplitude and frequency of underlying waves is not very different from supposing that the pressure, rarefaction, and temperature in substances originate in the distribution and motion of underlying molecules. Perrin, with his own eyes, had verified the motions presupposed by the kinetic theory in the diffusion, distribution, displacement, and rotational motion of granules. These motions *explained* the laws of emulsions, which were an extension of the gas laws. Even though Duhem saw no place for explanation in science, he conceded that in rare cases we have sufficient access so that the cause is laid bare, as he would say [Duhem, p. 47]. The Brownian movement was one such case.

Duhem remarked in *Aim and Structure* that when conflict between competing theories is settled in favor of one of the theories, resistance to the favored theory does not vanish right away. Proponents of the defeated theory might cling to their outdated view, and there is possibility of lengthy quarrels between the adherents of an old system and the partisans of a new doctrine. Duhem says, “The history of physics would furnish us with innumerable illustrations of these quarrels at all times and in all domains” [Duhem, pp. 217-218]. His view accords with Einstein’s description of the skeptics’ response to

Perrin's work on the Brownian movement. Commenting on the molecular-kinetic theory of heat and its confirmation in the first decade of the twentieth century, he said:

The agreement of these considerations with [Perrin's] experience together with Planck's determination of true molecular size from the law of radiation (for high temperatures) convinced the skeptics, who were quite numerous at the time (Ostwald, Mach) of the reality of atoms. The antipathy of these scholars towards atomic theory can indubitably be traced back to their positivistic philosophical attitude. This is an interesting example of the fact that even scholars of audacious spirit and fine instinct can be obstructed by the interpretation of facts by philosophic prejudice. The prejudice – which has by no means died out in the meantime – consists in the faith that facts by themselves can and should yield scientific knowledge without free conceptual construction [Einstein 1949, p. 49].

In his 1913 *Examen logique de la théorie physique*, Duhem still referred to the atomic conception as a hypothetical knowledge of the nature of things. Brownian movement he apparently failed to mention [Nye, p. 166].

Mach, likewise, resisted the discreteness of matter. In the 1909 reprint of his essay on the principle of conservation of work, he reproached the widespread investigation into molecular motion. He wrote: "If, then, we are astonished at the discovery that heat is motion, we are astonished at something which has never been discovered. It is quite irrelevant for scientific purposes whether we think of heat as a substance or not". Einstein received a copy of this essay and responded to Mach as follows, enclosing copies of some of his own works: "Especially I ask you to glance at the paper on Brownian movement, since here there is a motion that one must believe to be *heat motion*" [Brush, pp. 35-36]. Mach also failed to comment on the Brownian movements [Nye, p. 168].

To be fair, the most ardent supporter of the Energetics doctrine, Wilhelm Ostwald, gracefully conceded the reality of atoms and molecules after reviewing Perrin's experimental work in 1908. The same, however, cannot be said of Duhem or Mach, who continued resisting the atomic theory indefinitely. Like Bas van Fraassen, they might have said that convergence did not necessarily establish the discreteness of matter. They would indeed be right on that point; but, as we have seen, convergence to establish discreteness was deeper than just numerical. The motion of granules was an extension of molecular motion in more ways than one. In addition, it was complemented by indirect measures of discreteness – in measurements of the elementary charge and alpha rays – and direct measures of discreteness – in the diffusion, distribution, displacement, and rotation of discrete granules.

## V: Conclusion

The foregoing puts us in a better position to answer the question posed at the beginning of the paper. *Did Perrin really put a proper end to the long struggle regarding the physical reality of molecules?*

The numerical convergence of  $N$  across thirteen different equations, which Perrin brought together in *Les Atomes*, was truly impressive. Convergence is typically considered the crux of the argument for molecular reality, but mere numerical convergence only construes  $N$  as a constant of proportionality. We find evidence for the discreteness of matter in the details of the experiments.

The verification of discreteness in measurements of the elementary charge and alpha particles was indirect evidence in this respect. Millikan gave evidence that there is a unique elementary charge and that all charges are composed of integral multiples of it. A mole of a monovalent ionic compound carries a Faraday's worth of charge. The extent to which each unit of charge is linked to its own mass, we have grounds to suppose that a mole of a monovalent ionic compound is composed of discrete units of mass that carry individual elementary charges. The mole, then, is an integral multiple of discrete charge-carriers or molecules. Similarly, Rutherford uniquely identified alpha rays as discrete helium ions. The extent to which we can count the number of these particles and link them to the amount of radium lost or helium produced, this is indirect support that the radium lost or the helium produced is a collection of discrete molecules.

The verification of discreteness in the diffusion, distribution, displacement, and rotational motion of granules had all the virtues of the indirect methods. In addition, the granules were visibly discrete. Moreover, the Brownian movement was an extension of

molecular movement. It seems to have met Duhem's criterion for the kind of motion supposed by a theory that we can see with our own eyes. The verification of the gas laws in the visible domain, i.e. the Brownian movement, verified the kinetic theory on ontology. This was direct evidence for the discreteness of matter. It was also the strongest evidence for a statistical interpretation of the second law of thermodynamics. Proponents of the Energetics doctrine had no reason *a priori* to give up their phenomenological view of thermodynamics and adopt the statistical interpretation. The seemingly eternal Brownian movement necessitated the statistical interpretation.

The convergence of  $N$  from these indirect and direct methods was most significant for the argument for the discreteness of matter. While the basic facts of chemistry are accommodated on the assumption of discreteness and the kinetic theory of gases predicts many laws, evidence for discreteness in directly measured parameters makes the strongest argument for the discreteness of matter. This standard may seem outrageous to some. Eyvind Wichmann says:

In view of such evidence<sup>65</sup> for the existence of atoms it is hard to understand a certain school of thought, which persisted until the turn of the century, and which rejected the atomic hypothesis on the grounds there was no *direct* (!) evidence that matter is made of atoms [Wichmann, p. 6].

Bas van Fraassen's observation is noteworthy here, that success on the kinetic theory does not legitimize the assumptions of the kinetic theory on ontology. Wichmann also seems to ignore that the kinetic theory was riddled with anomalies well into the twentieth

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<sup>65</sup> From chemistry and the kinetic theory of gases.

century. Chief among them was the problem of specific heats and the breakdown of the equipartition theorem.

As mentioned in the beginning, establishing the physical reality of molecules minimally amounts to establishing that matter is discrete. The liberation of discrete elementary charges, the emission of discrete alpha particles, and the movement of discrete granules comprise strong evidence in this respect. At the same time, discreteness was not established in isolation. A count of the above discrete parameters amounted to a count of molecules in a mole of a substance. The observation of granules was the most direct method of counting. Moreover, the Brownian movement experiments established other tenets of the kinetic theory such as the statistical law of the Gaussian distribution of displacements and the equipartition between translational and rotational motions of granules. Perrin said, “*The laws of perfect gases are thus applicable in all their details to emulsions*”. This also established the discreteness of matter.

There was a gratifying aspect to the resolution of the question of the physical reality of molecules. Perrin gave experimental proof of discreteness, which had been vainly sought for centuries, even millennia.<sup>66</sup> More importantly, the resolution of the question of the physical reality of atoms and molecules legitimized research on their internal structure. The Bohr Model came out in 1913, and much of the research in microphysics over the next century has been predicated on the physical reality of atoms and molecules.

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<sup>66</sup> See Ostwald’s quote on p. 59.

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