W. Gerhard Pohl *

The theory of Brownian motion — one hundred years old

ROBERT BROWN (1773–1858) discovered the phenomenon named after him in 1827.[1] He as a botanist studied pollen grains under the microscope and was probably angry that these small particles moved around, and could not be studied well. He soon found out that not only pollen grains but all sorts of small particles showed this irregular motion. Since no energy was supplied from outside the movement was apparently supported from internal energy, which could only be thermal energy.

Since the mid-nineteenth century several authors considered the kinetic theory of heat, developed by Clausius, Maxwell, Boltzmann and others, as a possible explanation of Brownian motion. But the potential complexity of the phenomenon was the main reason why it failed to become a key subject of the great works on the kinetic theory of heat. Since the 1870s several scientists pursued the idea that Brownian motion might be explained as the result of collisions between suspended particles and the molecules of the liquid. One of them was Siegmund Exner (1846–1926) a Viennese physiologist who published his observations in 1867.[2] He found that the motion stopped at low temperatures and increased with increasing temperature. The motion also depended on the viscosity of the solution (in glycerine e.g. it stopped completely). In 1900 Siegmund Exner's son the physicist Felix Maria Exner (1876–1930), who later became a famous meteorologist, continued the studies of his father.[3] He studied rubber-emulsions, and determined the velocity of particles with a diameter of 0.001 mm and smaller. He found that the velocity of these particles was around 0,003 mm/s and increased when the size of the particles decreased. When the temperature of the liquid was raised from 20°C to 70°C the velocity of the particles increased by about 60%. But the measured velocities were dramatically smaller than that calculated from the kinetic theory of heat. Much faster velocities were observed by Richard Zsigmondy (1865–1929)[4] in colloidal gold solutions. So by the turn of the century Brownian motion had emerged as a veritable challenge to classical physics, even if this was not acknowledged by the majority of the physical community.

The first serious theoretical treatments of the Browninan motion was given in 1905 by Albert Einstein (1879–1955) and in 1906 by Marian von Smoluchowski, Ritter von Smolan (1872–1917). Following these pioneering papers several eminent physicists were concerned with further theoretical and experimental work on Brownian motion. An overview is given in the following paragraphs.

In 1898 Felix Exner attended lectures in mathematics[5] given by Marian von Smoluchowski. I don't know if there was a closer contact between these two young scientists at that time. The biography of Marian von Smoluchowski is described in the paper of Hermann Hunger.[6] I want to present some additional material from the archives of the University of Vienna. Among the teachers of Smoluchowski were Josef Stefan and Franz Exner (1849–1926), a brother of Siegmund Exner and uncle of Felix Exner. Smoluchowski also attended lectures of the chemist Adolf von Lieben (1836–1914) who initiated the Ignaz-Lieben-prize of the Austrian Academy of Sciences in 1865. The Lieben-prize was a model for the Nobel-prize. Smoluchowski's doctoral theses had the title "Akustische Untersuchungen

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[1] Brown, Robert, *Pogg. Annalen* 14, (1828), 294.

[2] Exner, Siegmund, *Sitzungsberichte der kaiserlichen Akademie der Wissenschaften Wien*, 56 (1867), 116.

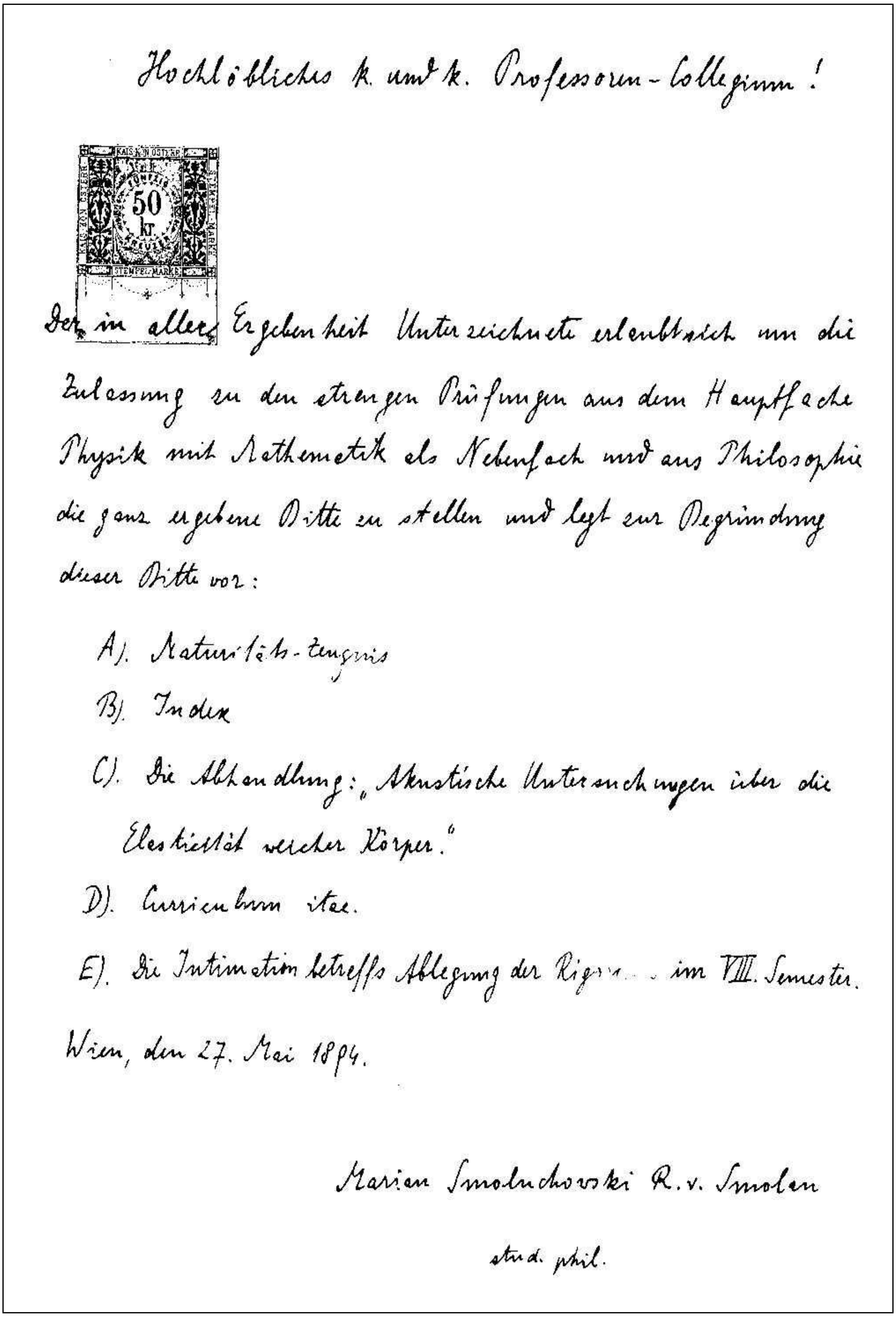
[3] Exner, Felix, *Annalen der Physik* 2 (1900), 843.

[4] Zsigmondy, Richard, *Zur Erkenntnis der Kolloide*, Jena 1905.

[5] Exner, Felix, Nationale WS 1898, *Archiv der Universität Wien*.

[6] Hunger, Hermann, "Smoluchowski and Vienna", in: M. Kokowski (ed.), *The Global and the Local: The History of Science and the Cultural Integration of Europe.* Proceedings of the 2nd ICESHS (Cracow, Poland, September 6–9, 2006), p. 412-415.

über die Elasticität weicher Körper" (Acustic studies of the elasticity of soft bodies). He passed his final exams in June and July 1894. His promotion occurred "sub auspiciis imperatoris" on May 15, 1895.



Hochlöbliches k. und k. Professoren-Collegium!

Der in aller Ergebenheit Unterzeichnete erlaubt sich um die Zulassung zu den strengen Prüfungen aus dem Hauptfache Physik mit Mathematik als Nebenfach und aus Philosophie die ganz ergebene Bitte zu stellen und legt zur Begründung dieser Bitte vor:

A). Maturitäts-Zeugnis

B). Index

C). Die Abhandlung: „Akustische Untersuchungen über die Elasticität weicher Körper."

D). Curriculum vitae.

E). Die Intimation betreffs Ablegung der Rigorosen im VIII. Semester.

Wien, den 27. Mai 1894.

Marian Smoluchowski R. v. Smolan

stud. phil.

Fig.1
Smoluchowski's application for the doctoral examinations
(from the archives of the University of Vienna)

When turning to the origins of Einstein's successful work on Brownian motion, one is confronted with a puzzle. He did not mention Brownian motion in the title of his paper,[7] which he evidently wrote without knowing that studies concerning Brownian motion had been conducted since many years.

5. *Über die von der molekularkinetischen Theorie der Wärme geforderte Bewegung von in ruhenden Flüssigkeiten suspendierten Teilchen; von A. Einstein.*

In dieser Arbeit soll gezeigt werden, daß nach der molekularkinetischen Theorie der Wärme in Flüssigkeiten suspendierte Körper von mikroskopisch sichtbarer Größe infolge der Molekularbewegung der Wärme Bewegungen von solcher Größe ausführen müssen, daß diese Bewegungen leicht mit dem Mikroskop nachgewiesen werden können. Es ist möglich, daß die hier zu behandelnden Bewegungen mit der sogenannten „Brownschen Molekularbewegung" identisch sind; die mir erreichbaren Angaben über letztere sind jedoch so ungenau, daß ich mir hierüber kein Urteil bilden konnte.

Wenn sich die hier zu behandelnde Bewegung samt den für sie zu erwartenden Gesetzmäßigkeiten wirklich beobachten läßt, so ist die klassische Thermodynamik schon für mikroskopisch unterscheidbare Räume nicht mehr als genau gültig anzusehen und es ist dann eine exakte Bestimmung der wahren Atomgröße möglich. Erwiese sich umgekehrt die Voraussage dieser Bewegung als unzutreffend, so wäre damit ein schwerwiegendes Argument gegen die molekularkinetische Auffassung der Wärme gegeben.

Fig.2.
First page of Einstein famous paper from 1905

He does not give any reference in his paper except one about Kirchhoff's "lectures on mechanics". In a letter to a friend Einstein wrote:

> on the assumption of the molecular theory of heat, bodies of the order of magnitude 0,001 mm, suspended in liquids, must already perform an observable random motion; in fact physiologists have observed unexplained motions of suspended small, inanimate bodies, which motions they designate as "Brownian molecular motion".

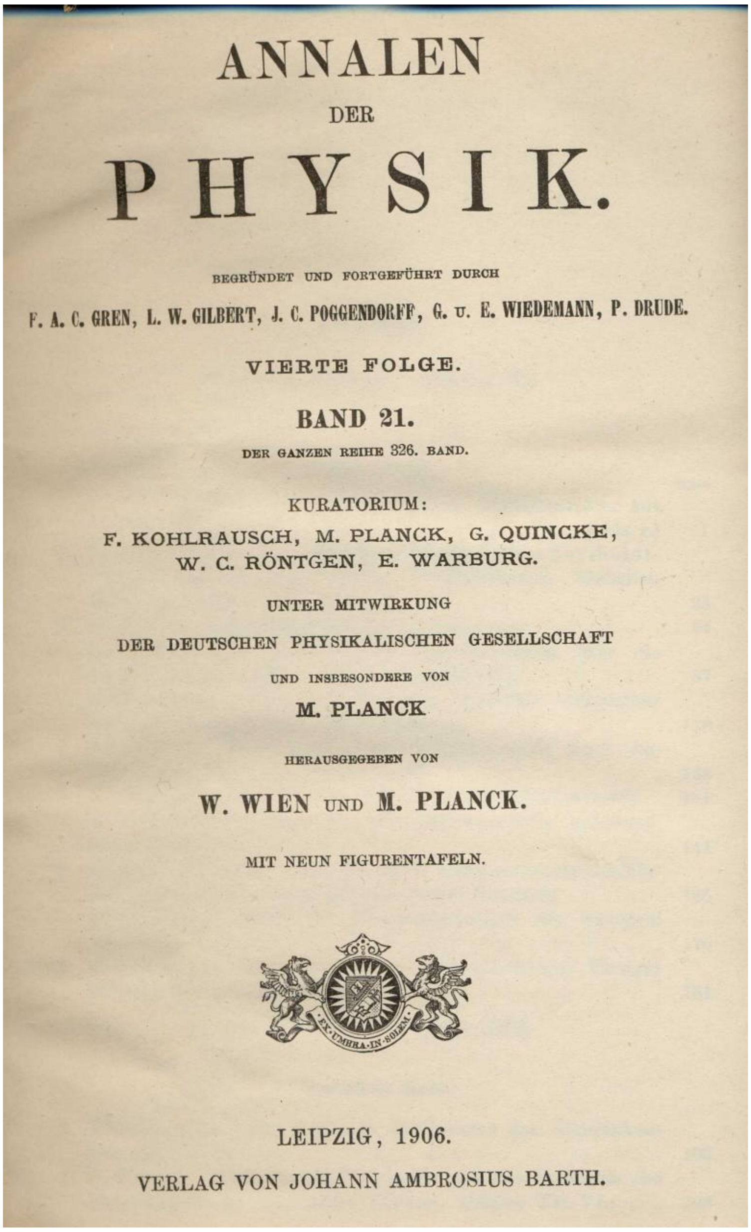
Einstein sent his paper to Ernst Mach, one of the sceptics with regard to atomism. In his autobiographical notes Einstein wrote (quote):

> The agreement of these considerations on Brownian motion with experience, together with Planck's determination of the true molecular size from the law of radiation convinced the sceptics, who were quite numerous at that time (Ostwald, Mach) of the reality of atoms.

The argument, that Brownian motion violates the second law of Thermodynamics, may has been the reason why Smoluchowski did not publish his earlier calculations on the subject. When he read

[7] Einstein, Albert, *Annalen der Physik* 17 (1905) 549.

Einstein’s paper he immediately decided to publish his results. 100 years ago in July 1906 Smoluchowski’s famous paper appeared in “Annalen der Physik”.[8]



ANNALEN
DER
PHYSIK.

BEGRÜNDET UND FORTGEFÜHRT DURCH
F. A. C. GREN, L. W. GILBERT, J. C. POGGENDORFF, G. u. E. WIEDEMANN, P. DRUDE.

VIERTE FOLGE.

BAND 21.
DER GANZEN REIHE 326. BAND.

KURATORIUM:
F. KOHLRAUSCH, M. PLANCK, G. QUINCKE,
W. C. RÖNTGEN, E. WARBURG.

UNTER MITWIRKUNG
DER DEUTSCHEN PHYSIKALISCHEN GESELLSCHAFT
UND INSBESONDERE VON
M. PLANCK

HERAUSGEGEBEN VON
W. WIEN UND M. PLANCK.

MIT NEUN FIGURENTAFELN.

EX UMBRA IN SOLEM

LEIPZIG, 1906.
VERLAG VON JOHANN AMBROSIUS BARTH.

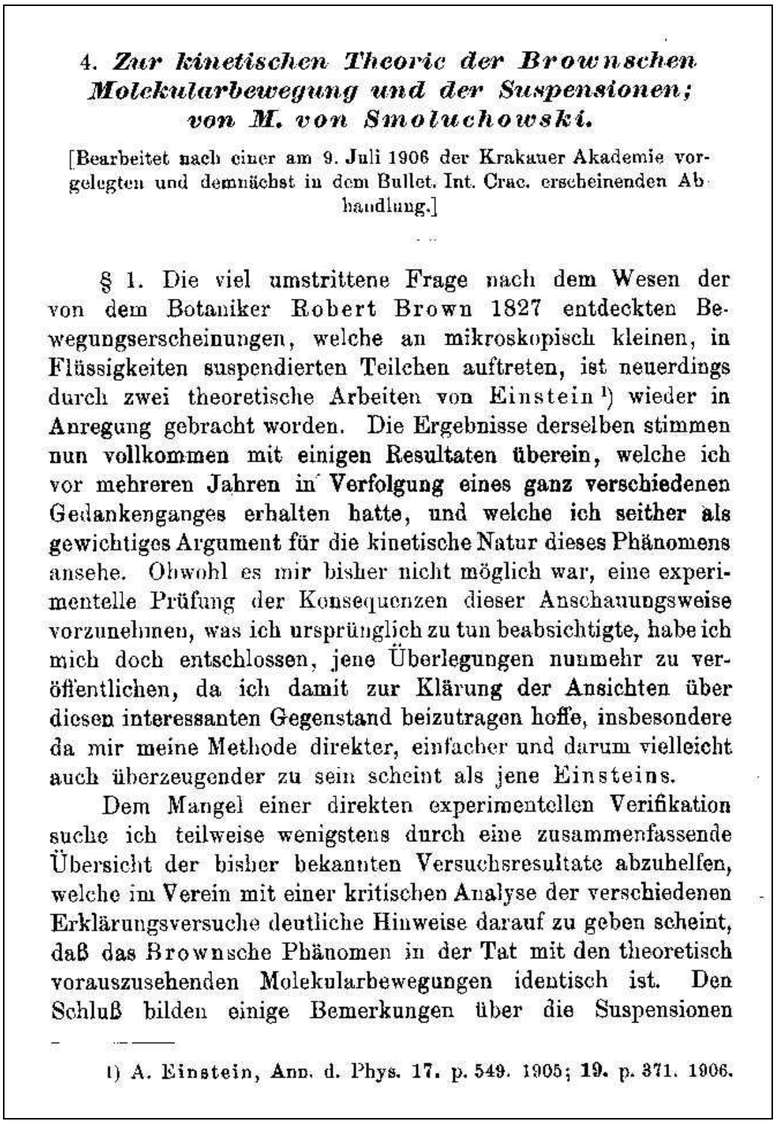
Fig.3.
In this volume Smoluchowski’s paper was published

At that time Smoluchowski was professor at the University of Lemberg (today Lviv, Ukraine). While Smoluchowski’s arguments were different and more direct as Einstein’s, his results were — apart from a numerical factor — essentially equivalent. The mean square of the displacement Δx^2 in the time τ of a particle with the radius r in a liquid of a viscosity η can be calculated using the gas-constant R, the absolute temperature T and Avogadro’s number N.

$$\Delta x^2 = \tau . RT / N 3 \pi \eta r \quad \text{in Einstein's treatment}$$

In Smoluchowski’s treatment we find an additional numerical factor 64/27 on the right hand side.

[8] von Smoluchowski, Marian, *Annalen der Physik* 21 (1906) 756.



4. ***Zur kinetischen Theorie der Brownschen Molekularbewegung und der Suspensionen; von M. von Smoluchowski.***

[Bearbeitet nach einer am 9. Juli 1906 der Krakauer Akademie vorgelegten und demnächst in dem Bullet. Int. Crac. erscheinenden Abhandlung.]

§ 1. Die viel umstrittene Frage nach dem Wesen der von dem Botaniker Robert Brown 1827 entdeckten Bewegungserscheinungen, welche an mikroskopisch kleinen, in Flüssigkeiten suspendierten Teilchen auftreten, ist neuerdings durch zwei theoretische Arbeiten von Einstein[1]) wieder in Anregung gebracht worden. Die Ergebnisse derselben stimmen nun vollkommen mit einigen Resultaten überein, welche ich vor mehreren Jahren in Verfolgung eines ganz verschiedenen Gedankenganges erhalten hatte, und welche ich seither als gewichtiges Argument für die kinetische Natur dieses Phänomens ansehe. Obwohl es mir bisher nicht möglich war, eine experimentelle Prüfung der Konsequenzen dieser Anschauungsweise vorzunehmen, was ich ursprünglich zu tun beabsichtigte, habe ich mich doch entschlossen, jene Überlegungen nunmehr zu veröffentlichen, da ich damit zur Klärung der Ansichten über diesen interessanten Gegenstand beizutragen hoffe, insbesondere da mir meine Methode direkter, einfacher und darum vielleicht auch überzeugender zu sein scheint als jene Einsteins.

Dem Mangel einer direkten experimentellen Verifikation suche ich teilweise wenigstens durch eine zusammenfassende Übersicht der bisher bekannten Versuchsresultate abzuhelfen, welche im Verein mit einer kritischen Analyse der verschiedenen Erklärungsversuche deutliche Hinweise darauf zu geben scheint, daß das Brownsche Phänomen in der Tat mit den theoretisch vorauszusehenden Molekularbewegungen identisch ist. Den Schluß bilden einige Bemerkungen über die Suspensionen

1) A. Einstein, Ann. d. Phys. **17.** p. 549. 1905; **19.** p. 371. 1906.

Fig.4.
First page of Smoluchowski's paper from 1906

On the other hand N can be calculated from known values of R, T, η, r and the measured Δx^2 during the time τ.

$$N = \tau RT / \Delta x^2 3 \pi \eta r$$

Paul Langevin (1872–1946) presented a third derivation in 1908[9] for the formula of the mean square of the displacement Δx^2. In his own words it is "infinitely more simple" than Einstein's. Langevin also showed that the numerical factor in Smoluchowski's derivation is due to certain assumptions. If these assumptions are corrected, the factor disappears. The mathematics of Langevin's derivation had great influence on the further development of "the new" physics.

Einstein's final request in his 1905-paper read (quote): "May soon a researcher be successful, to solve the question posed here, which is so important for the theory of heat." Also Smoluchowski had written in his paper, that he wanted to examine his theoretical thoughts by experiments.

Turning now to experimental results, we find that The Svedberg (1884–1971)[10] was the first to verify quantitatively the theories of Einstein and Smoluchowski without knowing their papers. His results

[9] Langevin, Paul, *C.R. Acad. Sci.* (Paris) 146, (1908), 530.

[10] Svedberg, *The, Zeitschrift f.Elektroch.* 12 (1906), 853, 909.

with different colloids proved that the mean square of displacement is proportional to the observation time and inversely proportional to the viscosity of the solution (at constant temperature):

$$\Delta x^2 = \text{const. } \tau / \eta$$

The quantitative treatment of the molecular kinetic theory of Brownian motion was tested in experiments by Jean Perrin (1870–1942) in 1908.[11] Perrin and his group started to pursue their experiments in line with Einstein's thinking on the subject. Then they tested a formula equivalent to that of Einstein and Smoluchowski for the vertical distribution of suspended particles under the influence of gravitation. They measured the sedimentation of different emulsions containing spherical particles of equal size with the microscope. Emulsions with particle diameters between 0,6 and 1,0 μ were investigated. The number of particles was counted at different heights in an equilibrated emulsion layer about 100 μ thick. Numbers which increased from top to bottom by sedimentation were counted stepwise in layers between 10 and 12 μ thick. It turned out that after equilibration the number of particles changed exponentially with the height in the liquid layer. From these measurements Perrin calculated Avogadro's number to be about $7{,}05 \times 10^{23}$. He compared it with numbers obtained by other methods which were between 4×10^{23} and 10×10^{23}. From these results Perrin concluded:

> finding that extremely different methods result in nearly the same values of N it is difficult when not impossible to be an opponent of the Molecular Hypothesis.

Perrin also followed the movement of single particles, marking their positions every 30 seconds. The real path of a particle is much more complicated than the zig-zag line obtained by connecting these marked positions. Values for the mean velocity of the particles were always a few microns per second for particle size of the order of one micron. Values of N calculated from these measurements were between 7×10^{23} and 8×10^{23}.

For particles in a colloid solution and for solutions of macromolecules the normal gravitational field is not strong enough to cause sedimentation. The Svedberg overcame this difficulty by developing the ultracentrifuge. At high gravitational fields he obtained sedimentation equilibria similar to those obtained by Perrin with larger particles. He showed that there is no principal difference between suspensions of particles of 1 micron size and solutions of macromolecules.

Following the experiments of Jean Perrin the Viennese physicist Felix Ehrenhaft (1879–1952) and his group studied Brownian motion experimentally under different conditions,[12] mainly in the gasous state. One of these systems was cigarette smoke. Ehrenhaft became wellknown because he had a fight with Robert Millikan (1868–1953) concerning the electrical charge of the electron.

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[11] Perrin, Jean, *Comptes rend.* 147 (1908), 1044.

[12] Ehrenhaft, Felix, *Sitzungsberichte der kaiserlichen Akademie der Wissenschaften Wien* 114 (1905), 1115; *Ibid.* 116 (1907), 1139, 1175.