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Article · May 2005

Source: arXiv

Norbert Straumann
University of Zurich

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Norbert Straumann
Institute for Theoretical Physics University of Zurich,
CH–8057 Zurich, Switzerland

February 2, 2008

Abstract

Einstein's thesis "A New Determination of Molecular Dimensions" was the second of his five celebrated papers in 1905. Although it is – thanks to its widespread practical applications – the most quoted of his papers, it is less known than the other four. The main aim of the talk is to show what exactly Einstein did in his dissertation. As an important application of the theoretical results for the viscosity and diffusion of solutions, he got (after eliminating a calculational error) an excellent value for the Avogadro number from data for sugar dissolved in water. This was in agreement with the value he and Planck had obtained from the black-body radiation. Two weeks after he finished the 'Doktorarbeit', Einstein submitted his paper on Brownian motion, in which the diffusion formula of his thesis plays a crucial role.

1 Introduction

When Einstein's great papers of 1905 appeared in print, he was not a newcomer in the *Annalen der Physik*, where he published most of his early work. Of crucial importance for his further research were three papers on the foundations of statistical mechanics, in which he tried to fill what he considered to be a gap in the mechanical foundations of thermodynamics. At the time when Einstein wrote his three papers he was not familiar with the work of Gibbs and only partially with that of Boltzmann. Einstein's papers form a bridge, parallel to the *Elementary Principles of Statistical Mechanics* by

*Talk given at the joint colloquium of ETH and the University of Zürich, 27 April (2005).

Gibbs in 1902, between Boltzmann's work and the modern approach to statistical mechanics. In particular, Einstein independently formulated the distinction between the microcanonical and canonical ensembles and derived the equilibrium distribution for the canonical ensemble from the microcanonical distribution. Of special importance for his later research was the derivation of the energy fluctuation formula for the canonical ensemble.

Einstein's profound insight into the nature and size of fluctuations played a decisive role for his most revolutionary contribution to physics: the light-quantum hypothesis. In this first paper of 1905 he extracted the light-quantum postulate from a statistical mechanical analogy between radiation in the Wien regime and a classical ideal gas of material particles. In this consideration Boltzmann's principle, relating entropy and probability of macroscopic states, played a key role. Later Einstein extended these considerations to an analysis of fluctuations in the energy and momentum of the radiation field. For the latter he was also drawing on ideas and methods he had developed in the course of his work on Brownian motion, another beautiful application of fluctuation theory. This definitely established the reality of atoms and molecules, and, more generally, gave strong support for the molecular-kinetic theory of thermodynamics.

Einstein's Doctoral thesis "A New Determination of Molecular Dimensions" was the second of his celebrated five papers in 1905. Unfortunately, it is not sufficiently well known. The main body of the paper is devoted to the hydrodynamic derivation of a relation between the coefficients of viscosity of a liquid with and without suspended particles. In addition, Einstein derived a novel formula for the diffusion constant D of suspended microscopic particles. This was obtained on the basis of thermal and dynamical equilibrium conditions, making use of van't Hoff's law for the osmotic pressure and Stokes' law for the mobility of a particle. Einstein then applied these two relations to sugar dissolved in water. Using empirical data he got (after eliminating a calculational error) an excellent value of the Avogadro number and an estimate of the size of sugar molecules. Einstein's thesis is the most quoted among his papers.

Soon afterwards Einstein's diffusion formula became also important in his work on Brownian motion. In this celebrated paper he first gave a statistical mechanical foundation of the osmotic pressure, and then repeated his earlier derivation in the thesis.

2 Biographical remarks

Einstein devoted his thesis to his friend Marcel Grossmann. Before I come to a technical discussion of the paper, I would like to give some biographical and other background.

Until 1909 the ETH was not authorized to grant doctoral degrees. For this reason a special arrangement enabled ETH students to obtain doctorates from the University. At the time most dissertations in physics by ETH students were carried out under the supervision of H.F. Weber, Einstein's former teacher at the 'Polytechnikum' as it was then called. The University of Zürich had only one physics chair, held by Alfred Kleiner. His main research was focused on measuring instruments, but he had an interest in the foundations of physics. From letters to Mileva one can see that Einstein often had discussions with Kleiner on a wide range of topics. Einstein also showed him his first dissertation in November 1901. This dissertation has not survived, and it is not really clear what it contained. At any rate, Einstein withdrew his dissertation in February 1902. One year later he was giving up his plan to obtain a doctorate. To Besso he wrote: "the whole comedy has become tiresome for me".

By March 1903 he seems to have changed his mind. Indeed, a letter to Besso contains some of the central ideas of the 1905 dissertation, especially in the second part of the following quote:

> "*Have you already calculated the absolute magnitude of ions on the assumption that they are spheres and so large that the hydrodynamical equations for viscous fluids are applicable? With our knowledge of the absolute magnitude of the electron [charge] this would be a simple matter indeed. I would have done it myself but lack the reference material and the time; you could also bring in diffusion in order to obtain information about neutral salt molecules in solution.*"

Kleiner was, of course, one of the two faculty reviewers of the dissertation, submitted by Einstein to the University on 20 July, 1905. His judgement was very positive: "the arguments and calculations to be carried out are among the most difficult in hydrodynamics". The other reviewer, Heinrich Burkhardt, Professor for Mathematics at the University, added: "the mode of treatment demonstrates *fundamental mastery of the relevant mathematical methods.*"

In his biography of Einstein, Carl Seelig reports: "Einstein later laughingly recounted that his dissertation was first returned by Kleiner with the comment that it was too short. After he had added a single sentence, it was accepted without further comment."

The physical reality of atoms was not yet universally accepted by the end of the nineteenth century. Fervent opponents were Wilhelm Ostwald and Georg Helm (who called themselves "energeticists"), and Ernst Mach admitted only that atomism may have a heuristic or didactic utility.

In his first three papers of 1905, Einstein found three different methods of determining the Avogadro number. (A few years later he found another one in his study of critical opalescence.) For him this was not only important for establishing the existence of atoms. He later wrote to Perrin:

> "*A precise determination of the size of molecules seems to me of the highest importance because Planck's radiation formula can be tested more precisely through such a determination than through measurements on radiation.*"

3 Einstein's dissertation

By 1905 several methods for determining molecular sizes were developed. The most reliable ones were based on kinetic theory of gases. An important early example is Loschmidt's work from 1865.[1] The following introductory remarks in Einstein's dissertation indicate what he adds to this.

> "*The earliest determinations of real sizes of molecules were possible by the kinetic theory of gases, whereas the physical phenomena observed in liquids have thus far not served for the determination of molecular sizes. This is no doubt due to the fact that it has not yet been possible to overcome the obstacles that impede the development of a detailed molecular-kinetic theory of liquids. It will be shown in this paper that the size of molecules of substances dissolved in an undissociated dilute solution can be obtained from the internal friction of the solution and the pure solvent, and from the diffusion of the dissolved substance within the solvent. (...).*"

Beside originality and intuition, great scientists usually also dispose of a fair amount of technical abilities. That Einstein was not an exception in this respect, should become clear if we now go into the technical details of his dissertation.

[1] J. Loschmidt, Wiener Ber. **52**, 395 (1866). See also J.C. Maxwell, *Collected Works*, Vol. 2, p. 361.

3.1 Basic equations of hydrodynamics

Let me first recall some general facts of hydrodynamics, that we shall need. I will use notation that has become standard, and not the one that was common at the time when Einstein did his work.

For stationary incompressible flows of homogeneous fluids, the Navier-Stokes equation is

$$(\mathbf{v} \cdot \nabla)\mathbf{v} = -\frac{1}{\rho}\nabla p + \frac{\eta}{\rho}\triangle\mathbf{v}.$$

We consider only situations with small Reynold numbers.Then one can neglect the left-hand side, and the basic equations become

$$\nabla p = -\eta\triangle\mathbf{v}, \quad \nabla \cdot \mathbf{v} = 0. \tag{1}$$

These imply that the pressure is harmonic: $\triangle p = 0$. The same holds for the vorticity curl $\mathbf{v}$. We also recall the expression for the stress tensor

$$\sigma_{ij} = -p\delta_{ij} + \eta(\partial_i v_j + \partial_j v_i). \tag{2}$$

According to (1) this is divergence-free: $\partial_j \sigma_{ij} = 0$. Later we shall also need the following expression for the rate W at which the stresses do work on the surface $\partial\Omega$ bounding a region Ω:

$$W = \int_{\partial\Omega} v_i \sigma_{ij} n_j \; dA. \tag{3}$$

Here, $\mathbf{n}$ is the outward pointing unit vector.

3.2 Einstein's strategy

With Einstein we now consider an incompressible fluid of viscosity η_0, in which a large number of identical, rigid, spherical particles is inserted. This suspension can be described in two ways: (1) On large scales, in comparison to the average separation of neighboring solute particles, as a homogeneous medium with an effective viscosity η. (2) By the stationary flow of the fluid (solvent) that is modified by the suspended particles.

For both descriptions Einstein computes according to (3) the rate of work for a big region Ω and obtains by equating the two results the important formula

$$\eta = \eta_0 \left(1 + \frac{5}{2}\varphi\right), \tag{4}$$

where φ denotes the fraction of the volume occupied by the suspended particles. This is assumed to be small (dilute suspension). (Due to a calculational error, Einstein originally lost the factor 5/2; we shall come back to this amusing story.)

3.3 Velocity field for a single suspended particle

We first adopt the second description. As a preparing task we have to determine the modification of a flow with constant velocity gradient, say, caused by a single little ball. Mathematically, we have to solve a boundary value problem for the elliptic system (1).

So let the unperturbed velocity field be

$$v_i^{(0)} = e_{ij} x_j, \tag{5}$$

where e_{ij} is a constant, symmetric, traceless tensor. The last property reflects the incompressibility. e_{ij} is the deformation tensor (we are not interested in flows with non-vanishing vorticity). The unperturbed pressure is denoted by $p^{(0)}$. The stress tensor for the background flow is

$$\sigma_{ij}^{(0)} = -p^{(0)} \delta_{ij} + 2\eta_0 e_{ij}. \tag{6}$$

We decompose the modified velocity field $\mathbf{v}$ according to

$$\mathbf{v} = \mathbf{v}^{(0)} + \mathbf{v}^{(1)} \tag{7}$$

into an unperturbed part plus a perturbation $\mathbf{v}^{(1)}$. The boundary conditions are: $\mathbf{v} = 0$ on the ball with radius a and $\mathbf{v} = \mathbf{v}^{(0)}$ at infinity. Analogous decompositions are used for the pressure and the stresses:

$$p = p^{(0)} + p^{(1)}, \quad \sigma_{ij} = \sigma_{ij}^{(0)} + \sigma_{ij}^{(1)}, \tag{8}$$

where

$$\sigma_{ij}^{(1)} = -p^{(1)} \delta_{ij} + \eta_0 (\partial_i v_j^{(1)} + \partial_j v_i^{(1)}). \tag{9}$$

For W we then have the decomposition ($|\Omega|$= volume of Ω)

$$W = 2\eta_0 e_{ij} e_{ij} |\Omega| + e_{ik} \int_{\partial\Omega} \sigma_{ij}^{(1)} x_k n_j \, dA + \int_{\partial\Omega} v_i^{(1)} \sigma_{ij}^{(0)} n_j \, dA. \tag{10}$$

The rigid ball is taken as the origin of a cartesian coordinate system. Einstein determines the perturbations $v_i^{(1)}$ and $p^{(1)}$ with the help of a method which is described in Kirchhoff's "Vorlesungen über Mechanik"[2], which he had studied during his student years. This involves the following two steps: a) Determine a function V, which satisfies the equation

$$\triangle V = \frac{1}{\eta_0} p^{(1)}, \tag{11}$$

[2]G. Kirchhoff, *Vorlesungen über mathematische Physik*, Vol. 1, *Mechanik*, Teubner (1897).

and set

$$v_i^{(1)} = \partial_i V + v'_i, \tag{12}$$

where v'_i has to satisfy the following equations

$$\triangle v'_i = 0, \quad \partial_i v'_i = -\frac{1}{\eta_0} p^{(1)}. \tag{13}$$

Remark on a). As a consequence of (11)-(13) the basic equations for $v_i^{(1)}$ and $p^{(1)}$ are satisfied:

$$\eta_0 \triangle v_i^{(1)} = \eta_0 \partial_i \triangle V = \partial_i p^{(1)}, \quad \partial_i v_i^{(1)} = \triangle V + \partial_i v'_i = 0.$$

b) Use the following decaying harmonic ansatz for $p^{(1)}$

$$\frac{p^{(1)}}{\eta_0} = A e_{ij} \partial_i \partial_j \left(\frac{1}{r}\right) \tag{14}$$

with a constants A, and try for v'_i the harmonic expression

$$v'_i = -\tilde{A} e_{ik} \partial_k \left(\frac{1}{r}\right) + B \partial_i e_{jk} \partial_j \partial_k \left(\frac{1}{r}\right). \tag{15}$$

This fulfills both equations (13) for $\tilde{A} = A$, because we then have

$$\partial_i v'_i = -A e_{ik} \partial_i \partial_k \left(\frac{1}{r}\right) = -\frac{p^{(1)}}{\eta_0}.$$

As a result of $\triangle r = 2/r$, equation (11) is satisfied for

$$V = \frac{1}{2} A e_{ij} \partial_i \partial_j r. \tag{16}$$

Performing the differentiations in (15) and (16), we obtain

$$v_i^{(1)} = \frac{3}{2} A e_{jk} \frac{x_i x_j x_k}{r^5} + B \left(6 e_{ik} \frac{x_k}{r^5} - 15 e_{jk} \frac{x_i x_j x_k}{r^7}\right). \tag{17}$$

The boundary condition $v_i^{(1)} = -e_{ij} x_j$ for $r = a$ requires

$$A = -\frac{5}{3} a^3, \quad B = -\frac{a^5}{6}. \tag{18}$$

We thus obtain for the perturbation of the velocity field ($n_i := x_i/r$)

$$v_i^{(1)} = -\frac{5}{2} a^3 e_{jk} \frac{1}{r^2} n_i n_j n_k - \frac{a^5}{6} \left(6 e_{ik} \frac{x_k}{r^5} - 15 e_{jk} \frac{x_i x_j x_k}{r^7}\right). \tag{19}$$

According to (12) and (15) for $\tilde{A} = A$ we can represent $v_i^{(1)}$ also as follows

$$v_i^{(1)} = -\frac{5}{6}a^3 e_{jk}\partial_i\partial_j\partial_k(r) + \frac{5}{3}a^3 e_{ik}\partial_k\left(\frac{1}{r}\right) - \frac{1}{6}a^5\partial_i e_{jk}\partial_j\partial_k\left(\frac{1}{r}\right). \qquad (20)$$

Equation (14) gives for the pressure

$$p = p^{(0)} - 5\eta_0 a^3 e_{ij}\frac{n_i n_j}{r^3}. \qquad (21)$$

Einstein claims that it can be demonstrated that his solution of the boundary value problem is unique, but he gives only some indications of what he thinks is a proof. Apparently, he did not know that an elegant uniqueness proof for such problems was already given in 1868 by Helmholtz.[3] Consider for two solutions of the basic equations, for given velocity fields on the boundaries, the non-negative quantity $(\theta'_{ij} - \theta_{ij})(\theta'_{ij} - \theta_{ij})$, where $\theta'_{ij}, \theta_{ij}$ are the deformation tensors of the two velocity fields. It is easy to show that the integral of this function over the region outside the bodies must vanish. (Use partial integrations and the basic equations (1).) Therefore, $\theta'_{ij} = \theta_{ij}$. In other words, the deformation tensor for the difference $v'_i - v_i$ of the two velocity fields vanishes. This difference is thus a combination of a rigid translation and a rigid rotation. Because of the imposed boundary conditions, the two velocity fields must agree. The pressures for the two solutions are, therefore, also the same, up to an additive constant.

3.4 Two expressions for the rate W

In (10) we now choose for Ω a large ball K_R with radius R. In leading order only the first term of (19) contributes, and a routine calculation leads to the following expression for W in terms of the spherical moments

$$\overline{n_i n_j n_k n_l} := \frac{1}{4\pi}\int_{S^2} n_i n_j n_k n_l \, d\Omega = \frac{1}{15}(\delta_{ij}\delta_{kl} + \delta_{ik}\delta_{jl} + \delta_{il}\delta_{lk}),$$

$$\begin{aligned} W &= 2\eta_0 e_{ij}e_{ij}|\Omega| + 20\pi a^3\eta_0 e_{ik}\{3e_{rs}\overline{n_i n_k n_r n_s} - e_{is}\overline{n_s n_k}\} \\ &= 2\eta_0 e_{ij}e_{ij}\left\{|\Omega| + \frac{1}{2}\frac{4\pi}{3}a^3\right\}. \end{aligned}$$

This holds for a single ball. As long as the suspension is dilute, we obtain Einstein's (corrected) result

$$W = 2\eta_0 e_{ij}e_{ij}|\Omega|\left(1 + \frac{1}{2}\varphi\right). \qquad (22)$$

[3] H. Helmholtz, "Theorie der stationären Ströme in reibenden Flüssigkeiten", Wiss. Abh., Bd. I, S. 223.

Following Einstein, we now calculate the same quantity by adopting the first description of the suspension. For this we write the result (20) in the form

$$v_i = e_{ij}x_j + (e_{ik}\triangle - e_{jk}\partial_i\partial_j)\partial_k f, \tag{23}$$

with

$$f = -\frac{1}{2}Ar - \frac{B}{r} \tag{24}$$

(A and B have the earlier meaning (18)). When the contributions of all the suspended balls, with number density n, inside the ball K_R are summed, we obtain for the velocity field in K_R

$$v_i = e_{ij}x_j + (e_{ik}\triangle - e_{jk}\partial_i\partial_j)\partial_k F, \tag{25}$$

where

$$F(|\mathbf{x}|) = n\int_{K_R} f(|\mathbf{x}-\mathbf{x}'|)\, d^3x' = \frac{\pi}{3}nA\left(\frac{1}{10}r^4 - r^2R^2\right) - 2\pi nB\left(R^2 - \frac{1}{3}r^2\right). \tag{26}$$

From this one easily finds

$$v_i = e_{ij}x_j(1-\varphi). \tag{27}$$

Einstein obtained this result slightly differently. We can use it to obtain a second expression for W:

$$W = 2\eta e_{ij}e_{ij}|\Omega|(1-2\varphi). \tag{28}$$

Comparing (22) and (28) leads to the announced formula (4) due to Einstein.

3.5 Two relations between the Avogadro number and the molecular radius.

If the rigid balls are molecules, for instance sugar, then

$$\varphi = \frac{4\pi}{3}a^3\frac{N_A\rho_s}{m_s}, \tag{29}$$

where ρ_s is the mass density of the solute and m_s its molecular weight which were known to Einstein. In addition, there existed measurements of η/η_0 for dilute sugar solutions. Hence, Einstein obtained from (4) a relation between N_A and a.

Using available data, Einstein states the following.[4] "One gram of sugar dissolved in water has the same effect on the coefficient of viscosity as do small

[4] I give here the later numbers from 1911.

suspended rigid spheres of a total volume of 0.98 cm^3." On the other hand, the *density* of an aqueous sugar solution behaves experimentally as a mixture of water and sugar in dissolved form with a specific volume of 0.61 cm^3. (The latter is also the volume of one gram of solid sugar.) Einstein interprets the difference of the two numbers as due to an attachment of water molecules to each sugar molecule. The radius a in (29) is thus a "hydrodynamically effective radius" of the molecule, which takes the enlargement due to hydration into account.

Diffusion

In order to be able to determine the two quantities individually, Einstein searched for a second connection, and thereby found his famous diffusion formula. Its derivation is quite short, but "extremely ingenious" (A. Pais). It rests on thermal and mechanical equilibrium considerations.

Assume that a constant external force $\mathbf{f}$ acts on the the suspended particles. This causes a particle current of magnitude $n\mathbf{v}$, where n is the number density and $\mathbf{v}$ = the velocity of the particle current. In equilibrium this is balanced by the diffusion current $-D\nabla n$, D = diffusion constant. The velocity of the particle current is proportional to $\mathbf{f}$,

$$\mathbf{v} = b\mathbf{f}, \quad b : \textit{mobility}. \tag{30}$$

These considerations give us the (dynamical) equilibrium condition

$$D\nabla n = nb\mathbf{f}. \tag{31}$$

In thermal equilibrium, the external force is balanced by the gradient of the osmotic pressure. According to the law of van't Hoff[5] this means

$$\mathbf{f} = \frac{kT}{n}\nabla n. \tag{32}$$

Inserting this into the last relation leads to the simple formula

$$D = kTb. \tag{33}$$

For the mobility Einstein uses Stokes' relation

$$b = \frac{1}{6\pi\eta_0 a} \tag{34}$$

[5] According to this, the osmotic pressure p exerted by the suspended particles is exactly the same as if they alone were present as an ideal gas. In equilibrium we thus have $n\mathbf{f} = \nabla p = kT\nabla n$.

and obtains in this way his famous formula

$$D = \frac{kT}{6\pi\eta_0 a}, \quad k = \frac{R}{N_A} \tag{35}$$

(R = gas constant).

This was almost simultaneously discovered in Australia by William Sutherland.

A beauty of the argument is that the exterior force drops out. Similar equilibrium considerations between systematic and fluctuating forces were repeatedly made by Einstein.

3.6 Silence, a calculational error, late attention

By 1909 Perrin's careful measurements of Brownian motion led to a new value for Avogadro's number that was significantly different from the value Einstein had obtained from his thesis work, and also somewhat different from what he and Planck had deduced from black-body radiation. Einstein then drew Perrin's attention to his hydrodynamical method, and suggested its application to the suspensions studied by Perrin. Then Jacques Bancelin, a Pupil of Jean Perrin, checked Einstein's viscosity formula $\eta = \eta_0(1 + \varphi)$. Bancelin confirmed that there was an increase of the viscosity that was independent of the size of the suspended particles, and only depends on the total volume they occupy. However, he got a stronger increase. Initially, this increase was too steep; in the publication Bancelin gives the result $\eta = \eta_0(1 + 2.9\varphi)$.

On 27 December, 1910 Einstein wrote from Zürich to his former student and collaborator Ludwig Hopf about the puzzling situation, and then adds:

> "*I have checked my previous calculations and arguments and found no error in them. You would be doing a great service in this matter if you would carefully recheck my investigation. Either there is an error in the work, or the volume of Perrin's suspended substance in the suspended state is greater than Perrin believes.*"

Hopf indeed found an error in some differentiation process, and got the formula (4). Einstein communicated the result to Perrin, and published in (1911) a correction of his thesis in the *Annalen.* (By the way, this correction is the second most quoted paper of Einstein.) New experimental data for sugar solutions now gave the excellent value

$$N_A = 6.56 \times 10^{23} \tag{36}$$

for the Avogadro number, in good agreement with the results of other methods, in particular with Perrin's determination from the Brownian motion, for which he got the Nobel price in 1926. Both results were discussed by Perrin in his extensive report at the famous Solvay conference in 1911.

4 Final remarks

In his 'Autobiographical Notes' of 1949, what he called his 'necrology', Einstein only briefly describes his applications of classical statistical mechanics. The thesis is not mentioned at all. About the law of Brownian motion he says:

> "*The agreements of these considerations with experience together with Planck's determination of the true molecular size from the law of radiation (for high temperatures) convinced the sceptics, who were quite numerous at the time (Ostwald, Mach) of the reality of atoms. The antipathy of these scholars toward 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 in the interpretation of facts by philosophical prejudices.*"

Perrin's famous book "Les Atomes" of 1913, a classic of twentieth century physics[6], ends with the words:

> "*The atomic theory has triumphed. Until recently still numerous, its adversaries, at last overcome, now renounce one after another their misgivings, which were, for so long, both legitimate and undeniably useful.*"

Einstein's very decent value (36) is not quoted in Perrin's book. This indicates that Einstein's thesis was not widely appreciated in the early years. For this reason Einstein published in 1920 a brief note, drawing attention to his erratum from 1911, "which till now seems to have escaped the attention of all who work in this field".

Since Einstein was so fond of applying physics to practical situations, he would certainly have enjoyed hearing that his doctoral thesis found so many applications.

[6] A new edition of the original text has appeared in Flammarion (1991), ISBN 2-08-081225-4; for an English translation, see: J. Perrin, *Atoms*, Van Nostrand (1916).