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A. E.

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EINSTEIN'S DISSERTATION ON THE DETERMINATION OF MOLECULAR DIMENSIONS

I

Einstein submitted a dissertation to the University of Zurich in 1901, about a year after graduation from the ETH, but withdrew it early in 1902.[1] In a successful second attempt three years later, he combined the techniques of classical hydrodynamics with those of the theory of diffusion to create a new method for the determination of molecular sizes and of Avogadro's number, a method he applied to solute sugar molecules.[2] The dissertation was completed on 30 April 1905 and submitted to the University of Zurich on 20 July.[3] On 19 August 1905, shortly after the thesis was accepted, the *Annalen der Physik* received a slightly different version for publication.[4]

Einstein 1906c (Doc. 33), published half a year later as a supplement to *Einstein 1906a*, utilizes experimental data not previously available to recalculate the size of sugar molecules. In 1911, after Jacques Bancelin found a discrepancy between the results of his experiments and Einstein's predictions, a calculational error in *Einstein 1905j* (Doc. 15) was discovered. Traces of an unsuccessful attempt by Einstein to locate the error, preserved as marginalia and interlineations in an offprint of the paper, are discussed in the annotations to Doc. 15. A correction of the error, which was found by Ludwig Hopf, then a collaborator of Einstein, is published in *Einstein 1911d*. The correction was reiterated in *Einstein 1920* and integrated into the republication of Einstein's dissertation in *Einstein 1922*.[5]

II

By 1905 several methods for the experimental determination of molecular dimensions were available.[6] Although estimates of upper bounds for the sizes of microscopic constituents of matter had been discussed for a long time, the first reliable methods for determining molecular sizes were developed in the second half of the nineteenth century, based

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[1] For evidence of Einstein's submission of the dissertation, see the Receipt for the Return of Doctoral Fees, 1 February 1902 (Vol. 1, Doc. 132).

[2] See *Einstein 1905j* (Doc. 15). For a study of Einstein's dissertation, see *Pais 1982*, chap. 2, § 5.

[3] See Einstein to Rudolf Martin, 20 July 1905.

[4] The thesis was unanimously accepted by the Mathematics and Physics Faculty on 27 July 1905 (see Protokollbuch der Konferenz, Abteilung VI A, SzZE Bibliothek, Hs 1079:2). For the changes that Einstein made in the *Annalen* version, *Einstein 1906a*, see the notes to *Einstein 1905j* (Doc. 15).

[5] For an English translation of *Einstein 1922*, see *Einstein 1926*. For the history of *Einstein 1922*, edited by Reinhold Fürth, see the editorial note, "Einstein on Brownian Motion,". § I, p. 206. Some of Fürth's annotations for the 1922 edition (see *Fürth 1922)* have been utilized in these editorial notes.

[6] For a survey of the development of methods for the determination of molecular dimensions, see *Brush 1976*, pp. 75–78. For a contemporary survey, see *Meyer, O. E. 1899*, chap. 10.

on the kinetic theory of gases.[7] The study of phenomena as diverse as contact electricity in metals, the dispersion of light, and black-body radiation yielded new approaches to the problem of molecular dimensions.[8] Most of the methods available by the turn of the century gave values for the size of molecules and for Avogadro's number that are in more or less satisfactory agreement with each other.[9]

Although Einstein claimed that the method in his dissertation is the first to use phenomena in fluids in the determination of molecular dimensions,[10] the behavior of liquids plays a role in various earlier methods. For example, the comparison of densities in the liquid and gaseous states is an important part of Loschmidt's method, based on the kinetic theory of gases.[11] A method that depends entirely on the physics of liquids was known as early as 1816. Young's study of surface tension in liquids led to an estimate of the range of molecular forces,[12] and capillary phenomena were used later in several different ways to determine molecular sizes.[13]

A kinetic theory of liquids, comparable to the kinetic theory of gases, was not available, and the methods for deriving molecular volumes exclusively from the properties of liquids did not give very precise results.[14] Einstein's method, on the other hand, yields values comparable in precision to those provided by the kinetic theory of gases. While methods based on capillarity presuppose the existence of molecular forces, Einstein's central assumption is the validity of using classical hydrodynamics to calculate the effect of solute molecules, treated as rigid spheres, on the viscosity of the solvent in a dilute solution.[15]

Einstein's method is well suited to determine the size of solute molecules that are large compared to those of the solvent. In 1905 William Sutherland published a new method for determining the masses of large molecules that shares important elements with Einstein's.[16] Both methods make use of the molecular theory of diffusion that Nernst developed on the basis of Van 't Hoff's analogy between solutions and gases, and of Stokes's law of hydrodynamical friction.[17]

Sutherland was interested in the masses of large molecules because of the role they play in the chemical analysis of organic substances such as albumin.[18] In developing a new method for the determination of molecular dimensions, Einstein was concerned with several other problems on different levels of generality. An outstanding current problem of the theory of solutions was whether molecules of the solvent are attached to the molecules

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[7] See, in particular, *Loschmidt 1865*.

[8] For methods based on contact electricity and the dispersion of light, see *Thomson, W. 1870;* for the determinations of Avogadro's number from black-body radiation, see *Planck 1901b* and *Einstein 1905i* (Doc. 14).

[9] See, e.g., *Meyer, O. E. 1899*, chap. 10.

[10] See *Einstein 1905j* (Doc. 15), p. 5.

[11] See *Loschmidt 1865*.

[12] See *Young 1816*.

[13] For a survey, see *Meyer, O. E. 1899*, chap. 10, § 122. For Einstein's knowledge of work on capillarity, see the editorial note, "Einstein on the Nature of Molecular Forces," pp. 3–4.

[14] For a discussion of the values given by these methods, see *Meyer, O. E. 1899*, chap. 10, § 122.

[15] For a discussion of his other assumptions, see § IV.

[16] See *Sutherland 1905*. Sutherland first outlined his method in 1904 (see ibid., p. 781). For a discussion of Sutherland's method, see § IV.

[17] See *Nernst 1888*, *Van 't Hofs 1887*, and *Stokes 1845*.

[18] See *Sutherland 1905*, p. 781.

or ions of the solute.[19] Einstein's dissertation contributed to the solution of this problem.[20] He recalled in 1909:

> At the time I used the viscosity of the solution to determine the volume of sugar dissolved in water because in this way I hoped to take into account the volume of any ***attached*** water molecules.
>
> Ich habe seinerzeit zur Bestimmung des Volumens des in Wasser aufgelösten Zuckers deswegen die Viskosität der Lösung benutzt, weil ich so das Volumen eventuel ***angelagerter*** Wassermoleküle mit zu berücksichtigen hoffte.[21]

The results obtained in his dissertation indicate that such an attachment does occur.[22]

Einstein's concerns extended beyond this particular question to more general problems of the foundations of the theory of radiation and the existence of atoms. He later emphasized:

> 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.
>
> Eine präzise Bestimmung der Grösse der Moleküle scheint mir deshalb von höchster Wichtigkeit, weil durch eine solche die Strahlungsformel von Planck schärfer geprüft werden kann als durch Strahlungsmessungen.[23]

The dissertation also marked the first major success in Einstein's effort to find further evidence for the atomic hypothesis, an effort that culminated in his explanation of Brownian motion.[24] By the end of 1905 Einstein had published three independent methods for determining molecular dimensions, and in the following years he found several more.[25]

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[19] ***Bousfield 1905b***, a study of the relationship between the sizes of ions and the electrical conductivity of electrolytes, calls this the most important open problem of the theory of aqueous solutions (p. 257). For contemporary reviews of research on hydrates, including a history of this problem, see ***Washburn 1908*** and ***1909***, and ***Dhar 1914***.

[20] ***Einstein 1906a*** is cited in ***Washburn 1909***, p. 70, and in ***Herzfeld 1921***, p. 1025, as providing evidence for the existence of an association between a solute molecule and molecules of the solvent.

[21] Einstein to Jean Perrin, 11 November 1909. The importance of this problem for Einstein is confirmed by a letter that Einstein wrote to Ludwig Hopf before 12 January 1911, emphasizing the significance of his equation for the coefficient of viscosity, "because from viscosity one can learn something about the volume of ***dissolved*** molecules" ("weil man aus der Viskosität etwas erfahren kann über das Volumen ***gelöster*** Moleküle").

[22] See ***Einstein 1905j*** (Doc. 15), p. 18.

[23] Einstein to Jean Perrin, 11 November 1909.

[24] In his ***Autobiographical Notes,*** Einstein stated that his work on statistical mechanics, which preceded his dissertation, aimed at finding "facts . . . that would guarantee as much as possible the existence of atoms of definite finite size" ("Tatsachen . . . welche die Existenz von Atomen von bestimmter endlicher Grösse möglichst sicher stellten") ***(Einstein 1979***, p. 44; translation, p. 45). For further discussion of Einstein's interest in the problem of molecular dimensions, see the editorial notes, "Einstein on the Foundations of Statistical Physics," p. 46, and "Einstein on Brownian Motion," pp. 206–222.

[25] In addition to the method published in the dissertation, other methods for the determina-

Of all these methods, the one in his dissertation is most closely related to his earlier studies of physical phenomena in liquids.[26]

III

Einstein's efforts to obtain a doctoral degree illuminate some of the institutional constraints on the development of his work on the problem of molecular dimensions. Einstein's choice of a theoretical topic for a dissertation at the University of Zurich was quite unusual, both because it was theoretical and because a dissertation theme was customarily assigned by the supervising professor.[27] By 1900, theoretical physics was slowly beginning to achieve recognition as an independent discipline in German-speaking countries, but it was not yet established at either the ETH or the University of Zurich. A beginning had been made at the ETH soon after its founding, with the appointment of the German mathematical physicist, Rudolf Clausius.[28] His departure a decade later may have been hastened by lack of official sympathy for a too-theoretical approach to the training of engineers and secondary-school teachers, the primary task of the school.[29]

Clausius's successor—after the position had been vacant for a number of years—was H. F. Weber, who occupied the chair for Mathematical and Technical Physics from 1875 until his death in 1912. During the last two decades of the nineteenth century, he did original research, mainly in experimental physics and electrotechnology, including work on a number of topics that were important for Einstein's later research,[30] such as blackbody radiation, the anomalous low-temperature behavior of specific heats, and the theory of diffusion; but his primary interests were never those of a theoretical physicist.[31]

The situation of theoretical physics at the University of Zurich at the turn of the century was hardly better. Four other major Swiss universities either had two full professorships in physics or one full and one nontenured position, while Zurich had only one physics chair, held by the experimentalist Alfred Kleiner.[32]

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tion of molecular dimensions are presented in ***Einstein 1905i*** (Doc. 14) and ***Einstein 1905k*** (Doc. 16). For a discussion of Einstein's various methods, see ***Pais 1982***, pp. 94–95.

[26] For a discussion of these studies, see Vol. 1, the editorial note, "Einstein on Molecular Forces," pp. 264–266, and the editorial note in this volume, "Einstein on the Nature of Molecular Forces," pp. 3–8.

[27] See the reports on dissertations in physics submitted between 1901 and 1905 to the University of Zurich (Promotionsgutachten, SzZSa, U 110 e 7, 8, and 9).

[28] For an account of the beginning of theoretical physics at the ETH, see ***Jungnickel and McCormmach 1986a***, pp. 186–193; the first four of these pages discuss the Clausius appointment.

[29] According to the ETH's founding statute, the "task of the polytechnic school consists of . . . educating engineers theoretically and as far as possible practically" ("Die Aufgabe der polytechnischen Schule besteht darin: Techniker . . . theoretisch und so weit tunlich praktisch auszubilden"). Mathematics and the natural sciences are assigned the role of "auxiliary sciences" ("Hilfswissenschaften"). See ***Bundesgesez 1854***, article 2. For the preference for practical training by ETH students, see ***Jungnickel and McCormmach 1986a***, p. 193.

[30] For additional information about Weber's activities at the ETH, see Vol. 1, the editorial note, "Einstein as a Student of Physics, and His Notes on H. F. Weber's Course," pp. 60–62.

[31] See Vol. 1, Biographies, pp. 387–388, and ***Weiss 1912***.

[32] The four universities were Basel, Fri-

Since the ETH was not authorized to grant doctoral degrees until 1909,[33] a special arrangement enabled ETH students to obtain doctorates from the University of Zurich.[34] Most dissertations in physics by ETH students were prepared under Weber's supervision, with Kleiner as the second referee. As noted above, almost all physics dissertations prepared at the ETH and the University of Zurich between 1901 and 1905 were on experimental topics suggested to the students by their supervisor or at least closely related to the latter's research interests.[35] The range of topics was quite limited, and generally not at the forefront of experimental research. Thermal and electrical conductivity, and instruments for their measurement, were by far the most prominent subjects. General questions of theoretical physics, such as the properties of the ether or the kinetic theory of gases, occasionally found their way into examination papers (*Klausurarbeiten*),[36] but they were hardly touched upon in dissertations.

In the winter semester of 1900–1901, Einstein intended to work for a degree under Weber.[37] The topic may have been related to thermoelectricity, a field in which Einstein had shown an interest and in which several of Weber's doctoral students did experimental research.[38] After a falling out with Weber, Einstein turned to Kleiner for advice and comments on his work.[39]

Although Kleiner's research at this time focused on measuring instruments, he did have an interest in foundational questions of physics,[40] and Einstein's discussions with him covered a wide range of topics.[41] Einstein showed his first dissertation to Kleiner before submitting it to the university in November 1901.[42] This dissertation has not survived, and the evidence concerning its contents is somewhat ambiguous. In April 1901 Einstein wrote that he planned to summarize his work on molecular forces, up to that time mainly

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bourg, Geneva, and Lausanne. For a sober assessment of his university's physics teaching, see Hans Schinz, Dekan, Philosophical Faculty II of the University of Zurich, to Erziehungsdirektion, Canton of Zurich, 10 September 1901 (SzZSa, U 110 b 1, Nr. 25). On Kleiner, see Vol. 1, Biographies, p. 383.

[33] See *Guggenbühl 1955*, pp. 133–135.

[34] See *Promotionsordnung 1899*, p. 2.

[35] See note 27 above.

[36] See the examination papers included with the reports on dissertations cited in note 27.

[37] For evidence of Einstein's intention to prepare a doctoral thesis under Weber, see the Questionnaire for Municipal Citizenship Applicants, 11–26 October 1900 (Vol. 1, Doc. 82).

[38] For the topics of dissertations submitted to the University of Zurich, see the Promotionsgutachten, SzZSa, U 110 e 7, 8, and 9. For Einstein's interest in thermoelectricity, see Einstein to Mileva Marić, 10 October 1899 (Vol. 1, Doc. 58).

[39] Einstein blamed Weber for the failure of his attempt to obtain a position at the University of Göttingen in March 1901 (see Einstein to Mileva Marid, 23 March 1901 and 27 March 1901, Vol. 1, Docs. 93 and 94). Discussions with Kleiner are mentioned in Marić to Einstein, early November 1901 and 13 November 1901 (Vol. 1, Docs. 123 and 124), and in Einstein to Marić, 19 December 1901 (Vol. 1, Doc. 130).

[40] For surveys of Kleiner's research, see Vol. 1, Biographies, p. 383, and *Andenken/Kleiner 1916*. For evidence of Kleiner's interest in foundational questions, see, e.g., *Kleiner 1901*, pp. 21–23.

[41] For evidence of the range of Einstein's discussions with Kleiner, see Einstein to Mileva Marić, 19 December 1901 and 8 February 1902 (Vol. 1, Docs. 130 and 136).

[42] The dissertation was submitted to the University of Zurich on 23 November 1901 (see note 1). For evidence that Einstein had earlier submitted the dissertation to Kleiner, see Mileva Marić to Einstein, 13 November 1901 (Vol. 1, Doc. 124).

on liquids;[43] at the end of the year, Marić stated that he had submitted a work on molecular forces in gases.[44] Einstein himself wrote that it concerned "a topic in the kinetic theory of gases" ("ein Thema der kinetischen Theorie der Gase").[45] There are indications that the dissertation may have discussed Boltzmann's work on gas theory, as well as Drude's work on electron theory of metals.[46]

By February 1902 Einstein had withdrawn the dissertation, possibly at Kleiner's suggestion that he avoid a controversy with Boltzmann.[47] In view of the predominantly experimental character of the physics dissertations submitted to the University of Zurich at the time, lack of experimental confirmation for his theoretical results may have played a role in the decision to withdraw the thesis.[48] In January 1903 Einstein still expressed interest in molecular forces, but he stated that he was giving up his plan to obtain a doctorate, arguing that it would be of little help to him, and that "the whole comedy has become tiresome for me" ("mir die ganze Komödie langweilig geworden ist").[49]

Little is known about when Einstein started to work on the dissertation he completed in 1905.[50] By March 1903 some of the central ideas of the 1905 dissertation had already occurred to him.[51] Kleiner, one of the two faculty reviewers (*Gutachter*) of his disserta-

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[43] See Einstein to Marcel Grossmann, 14 April 1901 (Vol. 1, Doc. 100).

[44] See Mileva Marić to Helene Savić, 23 November–mid-December 1901 (Vol. 1, Doc. 125).

[45] Einstein to the Swiss Patent Office, 18 December 1901 (Vol. 1, Doc. 129).

[46] Einstein to Mileva Marić, 17 December (Vol. 1, Doc. 128), states that, if Kleiner accepts the dissertation, "we'll see what stance the fine Mr. Drude takes" ("wollen wir sehen, wie sich der saubere Herr Drude dazu stellt"). Einstein to Marić, 8 February 1902 (Vol. 1, Doc. 136), mentions that part of one of two works previously submitted to Kleiner deals with Boltzmann's book. For a discussion of possible relations between Einstein's interests in kinetic theory and the electron theory of metals, see the editorial note, "Einstein on the Foundations of Statistical Physics," pp. 45–46.

[47] See the Receipt for the Return of Doctoral Fees, 1 February 1902 (Vol. 1, Doc. 132). According to a biography by Einstein's son-in-law, Kleiner rejected "an essay on the kinetic theory of gases" Einstein had given him in 1901 "out of consideration to his colleague Ludwig Boltzmann, whose train of reasoning Einstein had sharply criticized" (*Kayser 1930*, p. 69). See the preceding note for evidence that Einstein may have criticized Drude in his dissertation.

[48] This is suggested by Einstein's emphasis on his inability to provide such experimental confirmation in ***Einstein 1902a*** (Doc. 2); see p. 814.

[49] Einstein to Michele Besso, 22 January 1903.

[50] According to ***Winteler-Einstein 1924***, p. 23, Einstein attempted to submit his work on the electrodynamics of moving bodies to the University of Zurich: "But the thing didn't seem quite right to the leading professors, as the wholly unknown author paid no heed to authority figures, even attacked them! So the work was simply rejected (irony of fate!) and the candidate saw himself compelled to write and submit another, more harmless work, on the basis of which he then obtained the title of Doctor Philosophiae" ("Allein die Sache schien den massgebenden Professoren nicht ganz geheuer, nahm doch der gänzlich unbekannte Verfasser keine Rücksicht auf die Meinung anerkannter Autoritäten, griff sie wohl gar noch an! So wurde die Arbeit schlechthin abgewiesen (Ironie des Schicksals!) u. der Kandidat sah sich gezwungen, eine andere harmlosere Abhandlung zu verfassen u. einzureichen, auf die hin er denn auch den Titel eines Doctor Philosophiae erhielt"). For a discussion of Einstein's contemporary work on the electrodynamics of moving bodies, see the editorial note, "Einstein on the Theory of Relativity," pp. 253–274.

[51] See Einstein to Michele Besso, 17 March 1903. The relationship of this letter to Einstein's dissertation is noted in ***Holton 1980***, p. 54. The letter is discussed in detail in the following section.

tion, acknowledged that Einstein had chosen the topic himself and pointed out that "the arguments and calculations to be carried out are among the most difficult in hydrodynamics" ("die Ueberlegungen und Rechnungen, die durchzuführen sind, gehören zu den schwierigsten der Hydrodynamik"). The other reviewer, Heinrich Burkhardt, Professor of Mathematics at the University of Zurich, added: "the mode of treatment demonstrates *fundamental mastery of the relevant mathematical methods*" ("die Art der Behandlung zeugt von *gründlicher Beherrschung der in Frage kommenden mathematischen Methoden*").[52] Although Burkhardt checked Einstein's calculations, he overlooked a significant error in them.[53] The only reported criticism of Einstein's dissertation was for being too short.[54]

Compared to the other topics of his research at the time, his hydrodynamical method for determining molecular dimensions was a dissertation topic uniquely suited to the empirically oriented Zurich academic environment. In contrast to the Brownian motion work, for which the experimental techniques needed to extract information from observations were not yet available, Einstein's hydrodynamical method for determining the dimensions of solute molecules enabled him to derive new empirical results from data in standard tables.

IV

Like Loschmidt's method based on the kinetic theory of gases, Einstein's method depends on two equations for two unknowns, Avogadro's number N and the molecular radius P.[55] The first of Einstein's equations (the second equation on p. 21 of *Einstein 1905j* [Doc. 15]) follows from a relation between the coefficients of viscosity of a liquid with and without suspended molecules (k^* and k, respectively),[56]

$$k^* = k(1 + \varphi) , \qquad (1)^{[57]}$$

where φ is the fraction of the volume occupied by the solute molecules. This equation, in turn, is derived from a study of the dissipation of energy in the fluid.

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[52] Both quotations are from the Gutachten über das Promotionsgesuch des Hrn. Einstein, 20–24 July 1905 (SzZSa, U 110 e 9).

[53] For a discussion of the discovery of this error and its correction, see § V.

[54] *Seelig 1960*, p. 112, reports: "Einstein later laughingly recounted that his dissertation was at first returned to him by Kleiner with the comment that it was too short. After he had added a single sentence, it was accepted without further comment") ("Lachend hat Einstein später erzählt, daß ihm seine Dissertation zuerst von Kleiner mit der Bemerkung zurückgeschickt wurde, sie sei zu kurz. Nachdem er noch einen einzigen Satz eingeschaltet hatte, sei sie stillschweigend angenommen worden").

[55] See *Loschmidt 1865*. In *Einstein 1905j* (Doc. 15), p. 5, the kinetic theory of gases is mentioned as the oldest source for the determination of molecular dimensions. Loschmidt's method is discussed in *Einstein 1915a*, p. 258.

[56] See § 1 and § 2 of *Einstein 1905j* (Doc. 15).

[57] This equation was later corrected; the error and the correct equation are discussed in § V. For later comments on the limitations of this equation, see Einstein to Hans Albert Einstein, before 13 December 1940; see also *Puis 1982*, p. 92.

Einstein's other fundamental equation (the third equation on p. 21 of ***Einstein 1905j*** [Doc. 15]) follows from an expression for the coefficient of diffusion D of the solute. This expression is obtained from Stokes's law for a sphere of radius P moving in a liquid, and Van 't Hoff's law for the osmotic pressure:

$$D = \frac{RT}{6\pi k} \cdot \frac{1}{NP} \tag{2}$$

where R is the gas constant, T the absolute temperature, and N Avogadro's number.

The derivation of eq. (1), technically the most complicated part of Einstein's thesis, presupposes that the motion of the fluid can be described by the hydrodynamical equations for stationary flow of an incompressible homogeneous liquid, even in the presence of solute molecules; that the inertia of these molecules can be neglected; that they do not affect each other's motions; and that they can be treated as rigid spheres moving in the fluid without slipping, under the sole influence of hydrodynamical stresses.[58] The hydrodynamic techniques needed are derived from ***Kirchhoff 1897***, a book that Einstein first read during his student years.[59]

Eq. (2) follows from the conditions for the dynamical and thermodynamical equilibrium of the fluid. Its derivation requires the identification of the force on a single molecule, which appears in Stokes's law, with the apparent force due to the osmotic pressure (see ***Einstein 1905j*** [Doc. 15], p. 20). The key to handling this problem is the introduction of fictitious countervailing forces. Einstein had earlier introduced such fictitious forces: they are used in ***Einstein 1902a*** (Doc. 2) to counteract thermodynamical effects in proving the applicability to diffusion phenomena of a generalized form of the second law of thermodynamics;[60] they are also used in his papers on statistical physics.[61]

Einstein's derivation of eq. (2) does not involve the theoretical tools he developed in his work on the statistical foundations of thermodynamics; he reserved a more elaborate derivation, using these methods, for his first paper on Brownian motion.[62] Eq. (2) was derived independently, in somewhat more general form, by Sutherland in 1905.[63] To deal with the available empirical data, Sutherland had to allow for a varying coefficient of sliding friction between the diffusing molecule and the solution.

The basic elements of Einstein's method—the use of diffusion theory and the application of hydrodynamical techniques to phenomena involving the atomistic constitution of

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[58] Einstein's derivation is only valid for Couette flow; a generalization to Poiseuille flow is given in ***Simha 1936***. For a discussion of Einstein's assumptions, see ***Pais 1982***, p. 90.

[59] See Einstein to Mileva Marić, 29 July 1900 and 1 August 1900 (Vol. 1, Docs. 68 and 69).

[60] For a discussion of this generalization, see the editorial note, "Einstein on the Nature of Molecular Forces," p. 8.

[61] See, in particular, ***Einstein 1902b*** (Doc. 3), § 10.

[62] This derivation, given in ***Einstein 1905k*** (Doc. 16), § 3, is cited in a footnote to ***Einstein 1905j*** (Doc. 15), p. 20, that was presumably added after the former paper had appeared. In the same paper, he also used eq. (2) to study the relation between diffusion and fluctuations.

[63] See ***Sutherland 1905***, pp. 781–782.

matter or electricity—can be traced back to his earlier work.[64] Einstein's previous work had touched upon most aspects of the physics of liquids in which their molecular structure is assumed to play a role, such as Laplace's theory of capillarity, Van der Waals's theory of liquids, and Nernst's theory of diffusion and electrolytic conduction.[65]

Before Einstein's dissertation, the application of hydrodynamics to phenomena involving the atomic constitution of matter or electricity was restricted to consideration of the effects of hydrodynamical friction on the motion of ions. Stokes's law was employed in methods for the determination of the elementary charge[66] and played a role in studies of electrolytic conduction.[67] Einstein's interest in the theory of electrolytic conduction may have been decisive for the development of some of the main ideas in his dissertation.[68] This interest may have suggested a study of molecular aggregates in combination with water, as well as some of the techniques used in the dissertation.

In 1903 Einstein and Besso discussed a theory of dissociation that required the assumption of such aggregates, the "hypothesis of ionic hydrates" ("Ionenhydrathypothese"), as Besso called it,[69] claiming that this assumption resolves difficulties with Ostwald's law of dilution.[70] The assumption also opens the way to a simple calculation of the sizes of ions in solution, based on hydrodynamical considerations. In 1902 Sutherland had considered a calculation of the sizes of ions on the basis of Stokes's formula, but rejected it as in disagreement with experimental data.[71] Sutherland did not use the assumption of ionic hydrates, which can avoid such disagreement by permitting ionic sizes to vary with such physical conditions as temperature and concentration.[72] The idea of determining the sizes of ions by means of classical hydrodynamics occurred to Einstein in 1903, when he proposed to Besso what appears to be just the calculation that Sutherland had rejected:

> 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 elec-

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[64] Einstein presumably had acquired a basic knowledge of diffusion in liquids from his study of *Violle 1893* (see Vol. 1, "Albert Einstein—Beitrag für sein Lebensbild," p. lxiv). Chapter 4 contains an extensive treatment of diffusion and osmosis.

[65] See Vol. 1, the editorial note, "Einstein on Molecular Forces," pp. 264–266, and, in this volume, the editorial note, "Einstein on the Nature of Molecular Forces," pp. 3–8.

[66] See *Townsend 1920*, pp. 209–214, for a review of the use of Stokes's law in the interpretation of experiments on the determination of atomic charges.

[67] For a contemporary discussion of the application of Stokes's law to electrolytic conduction, see *Bousfield 1905b*. For a later survey, see *Herzfeld 1921*, pp. 1011–1018.

[68] For evidence of this interest, see *Einstein 1902a* (Doc. 2) and Michele Besso to Einstein, 7–11 February 1903.

[69] See ibid.

[70] For a discussion of this law, its failure for strong electrolytes, and the resolution of this difficulty by the "hypothesis that the ions of an electrolyte consist of molecular aggregates in combination with water," see *Bousfield 1905a*, p. 563.

[71] In *Sutherland 1902*, Sutherland wrote: "Now this simple theory must have been written down by many a physicist and found to be wanting" (p. 167).

[72] This conclusion was drawn by Bousfield (see *Bousfield 1905b*, p. 264).

> tron [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.
>
> Hast Du die absolute Größe der Ionen schon ausgerechnet unter der Voraussetzung, daß dieselben Kugeln und so groß sind, daß die Gleichungen der Hydrodynamik reibender Flüssigkeiten anwendbar sind. Bei unserer Kenntnis der absoluten Größe des Elektrons wäre dies ja eine einfache Sache. Ich hätte es selbst gethan, aber es fehlt mir an Litteratur und Zeit; auch die Diffusion könntest Du heranziehen, um über die neutralen Salzmoleküle in Lösung Aufschluss zu erhalten.[73]

This passage is remarkable, because both key elements of Einstein's method for the determination of molecular dimensions, the theories of hydrodynamics and diffusion, are already mentioned, although the reference to hydrodynamics probably covers only Stokes's law. While a program very similar to the first of Einstein's proposals to Besso is pursued in ***Bousfield 1905a*, *1905b***,[74] Einstein's dissertation can be seen to be an elaboration of the second proposal, regarding diffusion and neutral salt molecules. Einstein may thus have been proceeding similarly to Nernst, who first developed his theory of diffusion for the simpler case of nonelectrolytes.[75] The study of sugar solutions could draw upon extensive and relatively precise numerical data on viscosity and the coefficient of diffusion,[76] avoiding problems of dissociation and electrical interactions.[77]

V

The results obtained with Einstein's method for the determination of molecular dimensions differed from those obtained by other methods at the time, even when new data taken from ***Landolt and Börnstein 1905*** were used to recalculate them. In his papers on Brownian motion, Einstein cited either the value he obtained for Avogadro's number, or a more standard one.[78] Only once, in ***Einstein 1908c*** (Doc. 50), did he comment on the uncertainty in the determination of this number.[79] By 1909 Perrin's careful measurements of Brownian motion produced a new value for Avogadro's number, significantly different

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[73] See Einstein to Michele Besso, 17 March 1903.

[74] For a critical evaluation of Bousfield's work, see ***Dhar 1914***, p. 64.

[75] See ***Nernst 1888***.

[76] The tables of data for sugar solutions in ***Landolt and Börnstein 1894*** and ***1905*** are extremely detailed.

[77] For a discussion of these problems, see ***Sutherland 1902***, pp. 167ff, and, for a later review, ***Dhar 1914***; for an account of the problem of internal friction in electrolytes, see also ***Herzfeld 1921***, pp. 1013–1018.

[78] In ***Einstein 1905k*** (Doc. 16), Einstein cited a value for Avogadro's number taken from the kinetic theory of gases; in ***Einstein 1907c*** (Doc. 40), he cited the value obtained in ***Einstein 1906c*** (Doc. 33); in ***Einstein 1908c*** (Doc. 50), he again cited a value close to that derived from gas theory.

[79] See ***Einstein 1908c*** (Doc. 50), p. 237, fn. 2.

from the values Einstein obtained from his hydrodynamical method and from Planck's black-body radiation law.[80] For Einstein, this discrepancy was particularly significant in view of what he regarded as the problematic nature of Planck's derivation of the radiation

In 1909 Einstein drew Perrin's attention to his hydrodynamical method for determining the size of solute molecules. He emphasized that this method allows one to take into account the volume of any water molecules attached to the solute molecules, and suggested its application to the suspensions studied by Perrin.[82] In the following year, an experimental study of Einstein's formula for the viscosity coefficients (eq. [1] above) was performed in Perrin's laboratory by Jacques Bancelin.[83] Bancelin studied uniform aqueous emulsions of gamboge, prepared with the help of Perrin's method of fractional centrifugation. Bancelin confirmed that the increase in viscosity does not depend on the size of the suspended particles, but only on the fraction of the total volume that they occupy. However, he found a value for the increased viscosity that differs significantly from Einstein's prediction.[84] Bancelin sent a report of his experiments to Einstein, apparently citing a value of 3.9 for the coefficient of φ in eq. (1), instead of the predicted value of 1.[85]

After an unsuccessful attempt to find an error in his calculations,[86] Einstein wrote to his student and collaborator Ludwig Hopf:[87]

> 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

[80] For Einstein's derivation of Avogadro's number from the law of black-body radiation, see *Einstein 1905i* (Doc. 14), pp. 136–137.

[81] See Einstein to Jean Perrin, 11 November 1909, quoted in § II. For a discussion of Einstein's views on the foundations of Planck's theory, see the editorial note, "Einstein's Early Work on the Quantum Hypothesis," pp. 137–138.

[82] Einstein wrote: "It would perhaps not be uninteresting to apply to your suspensions the method for determining the volume of the suspended substance from the coefficients of viscosity and to make a comparison with the results of your methods" ("Es wäre vielleicht nicht uninteressant, die Methode zur,Bestimmung des Volumens der suspendierten Substanz aus den Reibungskoeffizienten bei Ihren Suspensionen anzuwenden und mit den Resultaten Ihrer Methoden zu vergleichen") (Einstein to Jean Perrin, 11 November 1909).

[83] See Einstein to Jean Perrin, 12 January 1911 and *Bancelin 1911a* and *1911b*.

[84] For Einstein's value, see eq. (1).

[85] On 12 January 1911, Einstein wrote to Perrin: "You will in any case be familiar with Bancelin's report to me as well as with my reply" ("Der Bericht von Herrn Bancelin an mich sowie meine Antwort an ihn werden Ihnen jedenfalls bekannt sein"). This letter cites the value of 3.9 as Bancelin's result. In a letter to Hopf written shortly before, Einstein cited a value of 3.8 (see Einstein to Ludwig Hopf, before 12 January 1911). For further evidence of correspondence between Einstein and Bancelin, see also *Bancelin 1911a*, p. 1383.

[86] See *Einstein 1905j* (Doc. 15), note 14, for evidence of this attempt.

[87] Ludwig Hopf was Einstein's student at the University of Zurich. In the summer semester of 1910 he registered for Einstein's lectures on mechanics and kinetic theory of heat, and for his physics seminar (Student Files, SzZU, Kassa-Archiv). In the same year he published two joint papers with Einstein *(Einstein and Hopf 1910a*, and *1910b).*

> Perrin's suspended substance in the suspended state is greater than Perrin believes.
>
> Ich habe nun meine damaligen Rechnungen & Ueberlegungen geprüft und keinen Fehler darin gefunden. Sie würden sich sehr um die Sache verdient machen, wenn Sie meine Untersuchung seriös nachprüfen würden. Entweder ist ein Fehler in der Arbeit oder das Volumen von Perrins suspendierter Substanz ist in suspendiertem Zustande grösser als Perrin glaubt.[88]

Hopf found an error in the derivatives of the velocity components, which occur in the equations for the pressure components on p. 12 of Einstein's dissertation. After correction of this error, the coefficient of φ in eq. (1) becomes 2.5.[89]

By mid-January 1911 Einstein had informed Bancelin and Perrin of Hopf's discovery of the error in his calculations.[90] The remaining discrepancy between the corrected factor 2.5 in eq. (1) and Bancelin's experimental value of 3.9 led Einstein to suspect that there might also be an experimental error. He asked Perrin:

> Wouldn't it be possible that your mastic particles, like colloids, are in a swollen state?[91] The influence of such a swelling 3.9/2.5 would be of rather slight influence on Brownian motion, so that it might possibly have escaped you.
>
> Wäre es nicht möglich, dass Ihre Mastixteilchen nach Art von Kolloiden sich in gequollenem Zustand befinden? Der Einfluss einer derartigen Quellung 3,9/2,5 wäre ja auf die Brown'sche Bewegung von ziemlich geringem Einfluss, sodass er Ihnen möglicherweise entgangen sein könnte.[92]

On 21 January, Einstein submitted his correction (*Einstein 1911d*) for publication. He presented the corrected form of some of the equations in *Einstein 1905j* (Doc. 15), and

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[88] Einstein to Ludwig Hopf, before 12 January 1911.

[89] In 1926, M. Kunitz claimed to have found another error in Einstein's derivation of the equation for the coefficients of viscosity (see John Northoff to Einstein, 5 April 1926, and the enclosed preprint of an article by Kunitz, published as *Kunitz 1926)*. The supposed error is based on a misprint in *Einstein 1906a* (see *Kunitz 1926)*. In his reply, Einstein proposed experiments on suspensions "for which φ is known, in order to test binding of H_2O in solutions" ("bei welchen φ bekannt ist, um dann bei Lösungen Bindung von H_2O zu prüfen") (Einstein to John Northoff, after 5 April 1926).

[90] Einstein to Jean Perrin, 12 January 1911. See this letter and *Bancelin 1911a*, p. 1383, for evidence of a letter by Einstein to Bancelin.

[91] Einstein later explained some peculiarities of viscosity in colloidal solutions: "A significantly greater increase in viscosity occurs in certain colloidal solutions of relatively small concentration, there being no sharply defined viscosity coefficient. Firm connections between particles then arise, forming chains throughout the volume, which, however, constantly re-form and dissolve over time according to statistical laws" ("Bei gewissen kolloidalen Lösungen von relativ kleiner Konzentration tritt oft eine bedeutend grössere Erhöhung der Viskosität ein, wobei es überhaupt keinen scharf definierten Viskositäts-Koeffizienten gibt. Es liegen dann feste Verbindungen der Teilchen vor, die Ketten durch das ganze Volumen bilden, die aber im Laufe der Zeit nach statistischen Gesetzen sich beständig neu bilden und wieder lösen") (Einstein to Hans Albert Einstein, before 13 December 1940).

[92] Einstein to Jean Perrin, 12 January 1911.

recalculated Avogadro's number. He obtained a value of 6.56×10^{23} per mole, a value that is close to those derived from kinetic theory and Planck's black-body radiation formula.

Bancelin continued his experiments, with results that brought experiment and theory into closer agreement. Four months later, he presented a paper on his viscosity measurements to the French Academy of Sciences,[93] giving a value of 2.9 as the coefficient of φ in eq. (1). Bancelin also recalculated Avogadro's number by extrapolating his results for emulsions to sugar solutions, and found a value of 7.0×10^{23} per mole.

Einstein's dissertation was at first overshadowed by his more spectacular work on Brownian motion, and it required an initiative by Einstein to bring it to the attention of his fellow scientists.[94] But the wide variety of applications of its results ultimately made the dissertation one of his most frequently cited papers.[95]

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[93] See ***Bancelin 1911a***. The paper was presented on 22 May 1911. Bancelin later published an article in German on the same results. (see ***Bancelin 1911b***).

[94] As is indicated by Einstein's letter of 11 November 1909 to Jean Perrin, he apparently drew Perrin's and thus Bancelin's attention to his work.

[95] See ***Cawkell and Garfield 1980***.