Lecture III:

On Einstein's Doctoral Thesis

NS: physics/0504201

Doctoral Thesis of Einstein:

A New Determination of Molecular Dimensions

completed on: 30 April, 1905 (Bern);
submitted to the University on 20 July

Content

- *Relative Change of Viscosity of a Suspension*:

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

- *Diffusion*:

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

- Data for Sugar Solutions $\Rightarrow$

$$\boxed{N_A, \ a}$$

First Thoughts

Letter to Besso, 17 March 1903 contains some of the central ideas, especially in the second part:

> " *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.*"

Further Motivation

to Perrin, 11 November 1909:

> *"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."*

Beginning of introduction:

> *"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. (...)."*

Hydrodynamic Tools

Navier-Stokes equation for stationary, incompressible, homogeneous fluid:

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

basic equations for small Reynold numbers:

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

($\Rightarrow \triangle p = 0$). Stress tensor:

$$\sigma_{ij} = -p\delta_{ij} + \eta(\partial_i v_j + \partial_j v_i), \quad \partial_j \sigma_{ij} = 0.$$

Rate of work by the stresses on the surface $\partial\Omega$ of a domain Ω:

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

Einstein's strategy

Computes the rate of work W on a big region in two different ways:

(1) in treating the suspension on scales $\gg$ than the separation of the solute particles as a homogeneous medium;

(2) by determining the stationary flow of the fluid (solvent), modified by the suspended particles.

result (after correcting a calculational error):

$$\boxed{\eta = \eta_0(1 + 2.5\varphi)}$$

Velocity Field

unperturbed flow:

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

deformation tensor e_{ij} constant, symmetric, traceless; $\Rightarrow p^{(0)} = const$;

stress tensor for the background flow:

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

Perturbations:

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

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

Rate of work:

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

Einstein uses a *method of Kirchhoff*:
a) determine a function V, satisfying the equations

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

and set

$$v_i^{(1)} = \partial_i V + v_i', \tag{2}$$

where v_i' has to satisfy

$$\triangle v_i' = 0, \quad \partial_i v_i' = -\frac{1}{\eta_0} p^{(1)}. \tag{3}$$

Remark on a): then the basic equations for $v_i^{(1)}$ and $p^{(1)}$ are satisfied:

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

b) Make the decaying harmonic ansatz for $p^{(1)}$:

$$\frac{p^{(1)}}{\eta_0} = A e_{ij} \partial_i \partial_j \left(\frac{1}{r}\right) \tag{4}$$

with a constant A, and try for v_i' the harmonic expression

$$v_i' = -\tilde{A} e_{ik} \partial_k \left(\frac{1}{r}\right) + B \partial_i e_{jk} \partial_j \partial_k \left(\frac{1}{r}\right). \tag{5}$$

All equations are satisfied if $\tilde{A} = A$ and

$$V = \frac{1}{2} A e_{ij} \partial_i \partial_j r. \tag{6}$$

boundary condition: $\mathbf{v} = 0$ on ball with radius a $\Rightarrow$

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

$$\begin{aligned} v_i^{(1)} = -\frac{5}{6}a^3 e_{jk}\partial_i\partial_j\partial_k(r) &+ \frac{5}{3}a^3 e_{ik}\partial_k\left(\frac{1}{r}\right) \\ &- \frac{1}{6}a^5\partial_i e_{jk}\partial_j\partial_k\left(\frac{1}{r}\right); \end{aligned}$$

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

Two expressions for W

1. $(\Omega = K_R)$

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

for a single ball. For dilute suspension:

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

2. Consider suspension on large scales as homogeneous medium mit effective viscosity η; velocity field:

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

$$F(|\mathbf{x}|) = n\int_{K_R} f(|\mathbf{x}-\mathbf{x}'|)\ d^3x', \qquad f = -\frac{1}{2}Ar - \frac{B}{r};$$

$\Rightarrow$

$$v_i = e_{ij}x_j(1-\varphi),$$

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

comparison gives result of Einstein.

Rigid balls $\rightarrow$ molecules
(e.g. sugar), then

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

ρ_s=mass density of solute, m_s=molecular weight;

$\Rightarrow$ **relation between N_A and a.**

Data for aqueous sugar solutions $\Rightarrow$
1 gram of sugar dissolved in water behaves as

- with respect to η : $\varphi = 0.98\ cm^3$;

- with respect to the density: $\varphi = 0.61\ cm^3$.

Difference: attachment of water molecules to sugar molecules (hydration);
a: "hydrodynamically effective radius".

Diffusion

Assume action of constant external force $\mathbf{f}$ per particle $\rightarrow$ particle current $n\mathbf{v}$;
in equilibrium balanced by diffusion current $-D\nabla n$ (D=Diffusionskonstante);
velocity of particle current is proportional to $\mathbf{f}$,

$$\mathbf{v} = b\mathbf{f}, \qquad b : mobility.$$

$\rightarrow$ (dynamical) equilibrium condition:

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

In thermal equilibrium external force balanced by gradient of osmotic pressure; van't Hoff $\Rightarrow$

$$\mathbf{f} = \frac{kT}{n}\nabla n;$$

insert ($\mathbf{f}$ drops out!):

$$D = kTb.$$

Stokes:

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

$\Rightarrow$

$$\boxed{D = \frac{kT}{6\pi\eta_0 a}.}$$

Silence, a calculational error, late attention

1910: Jacques Bancelin checkes Einstein's viscosity formula: originally $\eta = \eta_0(1 + \varphi)$; finds $\eta = \eta_0(1 + 2.9\varphi)$.

27 December, 1910: Einstein from Zürich to Ludwig Hopf:

> *"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 finds error: $\eta = \eta_0(1 + 2.5\varphi)$.

"Das Neue in der Physik ist folgendes. Perrin hat durch einen jungen Physiker (Jacques Bancelin) die Viskosität von Mastixemulsionen experimentell untersuchen lassen. Er findet $\eta = \eta_0(1 + 3.8\varphi)$ *(...). Die Untersuchung wurde gemacht, um eine von mir abgeleitete Formel zu prüfen. Diese lautet aber* $\eta = \eta_0(1 + \varphi)$. *Die Sache ist wichtig, weil man aus der Viskosität etwas erfahren kann über das Volumen* gelöster *Moleküle. Ich habe nun meine damaligen Rechnungen und Überlegungen geprüft und keinen Fehler darin gefunden. Sie würden sich sehr um die Sache verdient machen, wenn Sie meine Untersuchungen seriös überprüfen würden. Entweder ist ein Fehler in meiner Arbeit oder das Volumen von Perrin's suspendierter Substanz ist in suspendiertem Zustand grösser als Perrin glaubt. Die Sache ist auch wegen Perrin's Hauptarbeit wichtig, in der er mit ähnlichen Suspensionen operierte."*

With correction and new data
for sugar solutions:

$$\boxed{N_A = 6.56 \times 10^{23}.}$$

(From black-body rad.: $N_A = 6.17 \times 10^{23}$;
today: 6.0225....)

Perrin's famous book "Les Atomes"
of 1913 ends with:

> "*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. (...)*"

> "*La théorie atomique a triomphé. Encore nombreux naguère, ses adversaires enfin conquis renoncent l'un après l'autre aux défiances qui, longtemps, furent légitimes et sans doute utiles. C'est au sujet d'autres idées que se poursuivra désormais le conflit des instincts de prudence et d'audace dont l'équilibre est nécessaire au lent progrès de la science humaine.* "

Einstein 1949 in ‘Autobiographical Notes’ (‘necrology’):

“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.”

Uniqueness for boundary value problem

Consider for two solutions v_i, v_i', with $\theta_{ij} = (\partial_i v_j + \partial_j v_i)/2$, etc:

$$\int (\theta'_{ij} - \theta_{ij})(\theta'_{ij} - \theta_{ij})\ dV =$$
$$\int (v_i' - v_i)(\theta'_{ij} - \theta_{ij}) n_j\ dA$$
$$-\frac{1}{2}\int (v_i' - v_i)\triangle(v_i' - v_i)\ dV$$
$$= -\frac{1}{2\rho}\int (v_i' - v_i)\partial_i(p' - p)\ dV$$
$$= -\frac{1}{2\rho}\int (p' - p)(v_i' - v_i) n_i\ dA = 0; \quad \Rightarrow \theta'_{ij} = \theta_{ij}.$$

Thus: $v_i' - v_i$ = rigid translation + rigid rotation; $\Rightarrow\ v_i' = v_i$.