A review of *A new determination of molecular dimensions* *by* Albert Einstein

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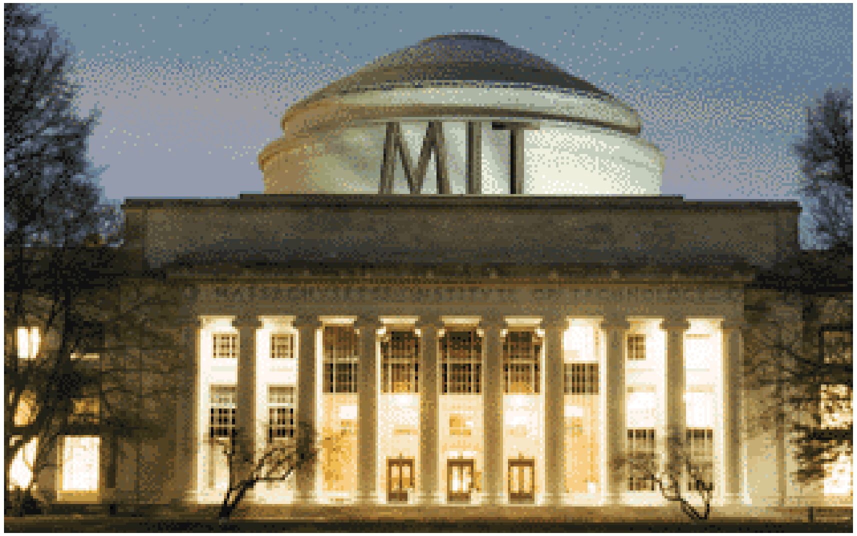


Einstein's Miraculous year: 1905

- the photoelectric effect: "On a Heuristic Viewpoint Concerning the Production and Transformation of Light", *Annalen der Physik* **17**: 132–148,1905 (received on March 18th).
- *A new determination of molecular dimensions*. This PhD thesis was completed on April 30th and submitted on July 20th, 1905. (*Annalen der Physik* 19: 289-306, 1906; corrections, 34: 591-592, 1911)
- Brownian motion: "On the Motion—Required by the Molecular Kinetic Theory of Heat—of Small Particles Suspended in a Stationary Liquid", *Annalen der Physik* **17**: 549–560,1905 (received on May 11th).
- special theory of relativity: "On the Electrodynamics of Moving Bodies", *Annalen der Physik* **17**: 891–921, 1905 (received on June 30th).
- mass-energy equivalence: "Does the Inertia of a Body Depend Upon Its Energy Content?", *Annalen der Physik* **18**: 639–641, 1905 (received September 27th).

Albert Einstein at his desk in the Swiss Patent office, Bern (1905)

References for viscosity of dilute suspensions

- Albert Einstein, *A new determination of molecular dimensions*. *Annalen der Physik* 19: 289-306, 1906; corrections, 34: 591-592, 1911 (English translation: Albert Einstein, Investigations on the theory of the Brownian movement, Edited with notes by R. FÜrth, translated by A.D. Cowper, Dover, New York, 1956)
- G. K. Batchelor, An introduction to fluid dynamics, p246 Cambridge University press, Cambridge, 1993
- Gary Leal, Laminar Flow and Convective Transport Processes Scaling Principles and Asymptotic Analysis, p175, Butterworth-Heinemann, Newton, 1992
- William M. Deen, Analysis of transport phenomena, p313, Oxford university press, 1998

outline

- In the presence of one particle

  1)velocity profile

  2)the rate of dissipation of mechanical energy
- In the presence f multiple particles

  1)velocity profile

  2)the rate of dissipation of mechanical energy

  3)viscosity
- Highly concentrated suspensions: beyond Einstein's formula
- An application: Calculate Avagadro number N using viscosity and diffusion coefficients

Motions of the liquid

Rigid body motions
- Parallel displacement
- rotation

Non rigid body motion
Straining motion

Transport momentum (Stress)

Principal dilatations

$$\nabla \underline{u} + (\nabla \underline{u})^T = \frac{1}{2}\begin{bmatrix} A & 0 & 0 \\ 0 & B & 0 \\ 0 & 0 & C \end{bmatrix}$$ ← (No body torque)

$$\underline{u} = [u_o \; v_o \; w_o]$$

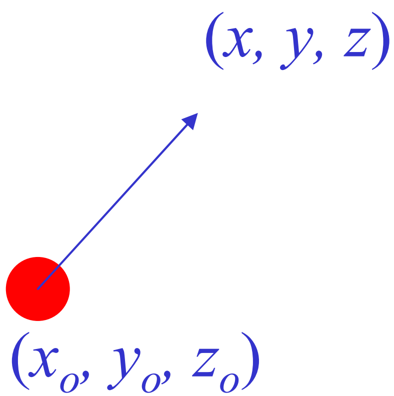
$$x - x_o = \xi \qquad u_o = A\xi$$
$$y - y_o = \eta \qquad v_o = B\eta$$
$$z - z_o = \zeta \qquad w_o = C\zeta$$

(x, y, z)

(x_o, y_o, z_o)

$$\nabla \cdot \underline{u} = A + B + C = 0$$ ← incompressibility

Governing equations and boundary conditions for the flow past a sphere



Navier-Stokes equation:

k: viscosity of the fluid

$$\rho[\cancel{\frac{\partial \underline{u}}{\partial t}} + \cancel{\underline{u}\cdot\nabla\underline{u}}] = \cancel{\rho\underline{g}} - \nabla p + k\nabla^2\underline{u}$$

Steady state No inertia Neglect gravity

$$\nabla p = k\nabla^2\underline{u} \quad \text{(Stokes equations)}$$

$$\nabla\cdot\underline{u} = 0 \quad \text{(Incompressibility)}$$

$$(4) \qquad \frac{\partial p}{\partial \xi} = k\Delta u, \frac{\partial p}{\partial \eta} = k\Delta v, \frac{\partial p}{\partial \zeta} = k\Delta w, \frac{\partial u}{\partial \xi} + \frac{\partial v}{\partial \eta} + \frac{\partial w}{\partial \zeta} = 0$$

B.C. $\quad u = v = w = 0$ *at the surface of the sphere*

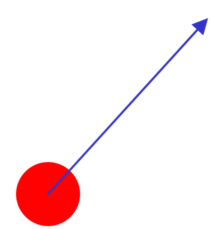
To find solutions (1)

Velocity without the presence of the particle

disturbance due to the particle

$$u = A\xi + u_1$$
$$v = B\eta + v_1$$
$$w = C\zeta + w_1$$

$$x - x_o = \xi$$
$$y - y_o = \eta$$
$$z - z_o = \zeta$$



$$u_1 \to 0$$
$$v_1 \to 0 \qquad as\ \rho \to \infty, \ \rho = \sqrt{\xi^2 + \eta^2 + \zeta^2}$$
$$w_1 \to 0$$

To find solutions (2)

The structure of $\underline{u}$:

$$u = \frac{\partial V}{\partial \xi} + u', v = \frac{\partial V}{\partial \eta} + v', w = \frac{\partial V}{\partial \zeta} + w' \qquad \text{with}$$

Harmonic functions

$$\nabla^2 u' = 0, \nabla^2 v' = 0, \nabla^2 w' = 0 \qquad \frac{\partial u'}{\partial \xi} + \frac{\partial v'}{\partial \eta} + \frac{\partial w'}{\partial \zeta} = -\frac{1}{k} p$$

and

$$\nabla^2 V = \frac{1}{k} p$$

Which satisfies the governing equations

$$k\nabla^2 u = k\nabla^2 (\frac{\partial V}{\partial \xi} + u') = k(\frac{\partial}{\partial \xi}\nabla^2 V + \nabla^2 u') = k\frac{\partial}{\partial \xi}(\frac{1}{k}p) + 0 = \frac{\partial p}{\partial \xi}$$

$$k\nabla^2 v = k\nabla^2 (\frac{\partial V}{\partial \eta} + v') = k(\frac{\partial}{\partial \eta}\nabla^2 V + \nabla^2 v') = k\frac{\partial}{\partial \eta}(\frac{1}{k}p) + 0 = \frac{\partial p}{\partial \eta}$$

$$k\nabla^2 w = k\nabla^2 (\frac{\partial V}{\partial \zeta} + w') = k(\frac{\partial}{\partial \zeta}\nabla^2 V + \nabla^2 w') = k\frac{\partial}{\partial \zeta}(\frac{1}{k}p) + 0 = \frac{\partial p}{\partial \zeta}$$

$$\Rightarrow \nabla p = k\nabla^2 \underline{u}$$

$$\frac{\partial u}{\partial \xi} + \frac{\partial v}{\partial \eta} + \frac{\partial w}{\partial \zeta} = \frac{\partial}{\partial \xi}(\frac{\partial V}{\partial \xi} + u') + \frac{\partial}{\partial \eta}(\frac{\partial V}{\partial \eta} + u') + \frac{\partial}{\partial \zeta}(\frac{\partial V}{\partial \zeta} + u')$$

$$= \nabla^2 V + \frac{\partial u'}{\partial \xi} + \frac{\partial v'}{\partial \eta} + \frac{\partial w'}{\partial \zeta} = \frac{1}{k}p - \frac{1}{k}p = 0$$

$$\Rightarrow \nabla \cdot \underline{u} = 0$$

To find solutions (3)

Governing equations

Harmonic function

$$\nabla^2 p = \nabla \cdot \nabla p = \nabla \cdot (k\nabla^2 \underline{u}) = k\nabla^2(\nabla \cdot \underline{u}) = 0$$

$$\frac{p}{k} = 2c\frac{\partial^2 \frac{1}{\rho}}{\partial \xi^2}$$

$$V = c\frac{\partial^2 \rho}{\partial \xi^2} + b\frac{\partial^2 \frac{1}{\rho}}{\partial \xi^2} + \frac{a}{2}(\xi^2 - \frac{\eta^2}{2} - \frac{\zeta^2}{2})$$

$$u' = -2c\frac{\partial \frac{1}{\rho}}{\partial \xi}, v' = 0, w' = 0$$

$$\frac{\partial^2 \frac{1}{\rho}}{\partial \xi^2} = \frac{3\xi^2}{\rho^5} - \frac{1}{\rho^3}$$

$$\frac{\partial^2 \frac{1}{\rho}}{\partial \eta^2} = \frac{3\eta^2}{\rho^5} - \frac{1}{\rho^3}$$

$$\frac{\partial^2 \frac{1}{\rho}}{\partial \zeta^2} = \frac{3\zeta^2}{\rho^5} - \frac{1}{\rho^3}$$

solutions for flow past a sphere

(5)

$$p = -\frac{5}{3} k P^3 \left\{ A \frac{\partial^2 \left(\frac{1}{\rho}\right)}{\partial \xi^2} + B \frac{\partial^2 \left(\frac{1}{\rho}\right)}{\partial \eta^2} + C \frac{\partial^2 \left(\frac{1}{\rho}\right)}{\partial \zeta^2} \right\} + \text{const.}$$

$$p = p' + const.$$

$$\frac{\partial^2 \frac{1}{\rho}}{\partial \xi^2} = \frac{3\xi^2}{\rho^5} - \frac{1}{\rho^3}$$

$$\frac{\partial^2 \frac{1}{\rho}}{\partial \eta^2} = \frac{3\eta^2}{\rho^5} - \frac{1}{\rho^3}$$

$$\frac{\partial^2 \frac{1}{\rho}}{\partial \zeta^2} = \frac{3\zeta^2}{\rho^5} - \frac{1}{\rho^3}$$

(6)

$$u = A\xi - \frac{5}{2}\frac{P^3}{\rho^5}\xi(A\xi^2 + B\eta^2 + C\zeta^2) + \frac{5}{2}\frac{P^5}{\rho^7}\xi(A\xi^2 + B\eta^2 + C\zeta^2) - \frac{P^5}{\rho^5}A\xi$$

$$v = B\eta - \frac{5}{2}\frac{P^3}{\rho^5}\eta(A\xi^2 + B\eta^2 + C\zeta^2) + \frac{5}{2}\frac{P^5}{\rho^7}\eta(A\xi^2 + B\eta^2 + C\zeta^2) - \frac{P^5}{\rho^5}B\eta$$

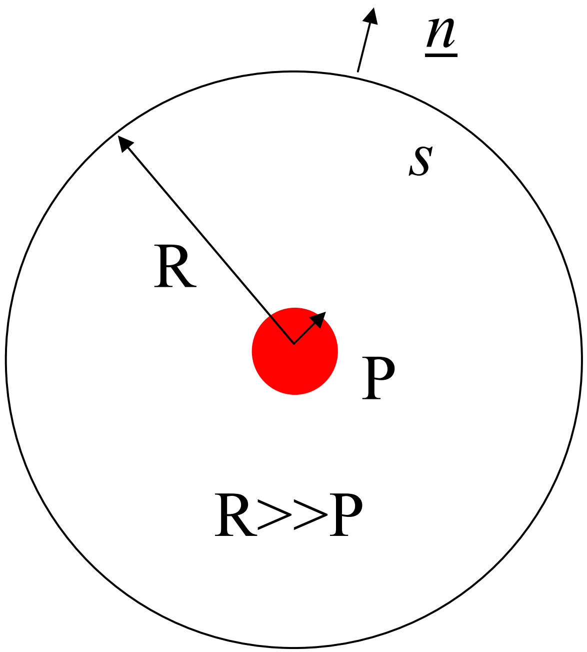
$$w = C\zeta - \frac{5}{2}\frac{P^3}{\rho^5}\zeta(A\xi^2 + B\eta^2 + C\zeta^2) + \frac{5}{2}\frac{P^5}{\rho^7}\zeta(A\xi^2 + B\eta^2 + C\zeta^2) - \frac{P^5}{\rho^5}C\zeta$$

$u_1 \to 0$

$v_1 \to 0$ and $p' \to 0$, as $\rho \to \infty$, $\rho = \sqrt{\xi^2 + \eta^2 + \zeta^2}$

$w_1 \to 0$

The rate of dissipation of mechanical energy



Force acting on the surface *s*

$$W = \int [\underline{\underline{t}}(\underline{n}) \cdot \underline{u}] ds = \int (\underline{n} \cdot \underline{\underline{t}}) \cdot \underline{u} ds$$

$$\underline{\underline{t}} = -p\underline{\underline{I}} + 2k\underline{\underline{E}}$$

$$\underline{\underline{E}} \equiv \frac{1}{2}[\nabla \underline{u} + (\nabla \underline{u})^T]$$

(P 46-48)

Neglect higher order terms

Extra mechanical work due to the particle

(7) $W = \frac{8}{3}\pi R^3 k\delta^2 + \frac{4}{3}\pi P^3 k\delta^2 = 2\delta^2 k\left(V + \frac{\Phi}{2}\right)$, (23)

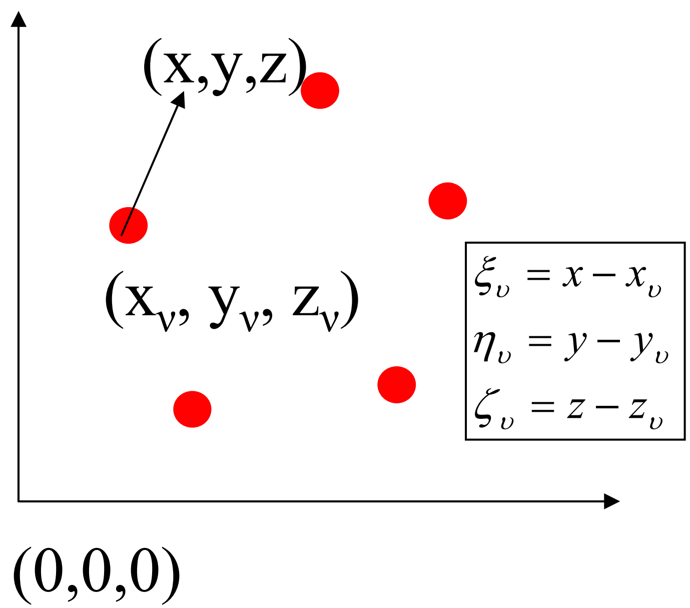
where we put

$$\delta^2 = A^2 + B^2 + C^2,$$

$$\frac{4\pi}{3}R^3 = V \text{ and } \frac{4}{3}\pi P^3 = \Phi$$

Pure fluid

With the presence of multiple particles



(8)

$$\begin{cases} u = Ax - \Sigma\left\{\frac{5}{2}\frac{P^3}{\rho_\nu^2}\frac{\xi_\nu(A\xi_\nu^2+B\eta_\nu^2+C\zeta_\nu^2)}{\rho_\nu^3} - \frac{5}{2}\frac{P^3}{\rho_\nu^4}\frac{\xi_\nu(A\xi_\nu^2+B\eta_\nu^2+C\zeta_\nu^2)}{\rho_\nu^3} + \frac{P^5}{\rho_\nu^4}\frac{A\xi_\nu}{\rho_\nu}\right\}, \\ v = By - \Sigma\left\{\frac{5}{2}\frac{P^3}{\rho_\nu^2}\frac{\eta_\nu(A\xi_\nu^2+B\eta_\nu^2+C\zeta_\nu^2)}{\rho_\nu^3} - \frac{5}{2}\frac{P^5}{\rho_\nu^4}\frac{\eta_\nu(A\xi_\nu^2+B\eta_\nu^2+C\zeta_\nu^2)}{\rho_\nu^3} + \frac{P^5}{\rho_\nu^4}\frac{B\eta_\nu}{\rho_\nu}\right\}, \\ w = Cz - \Sigma\left\{\frac{5}{2}\frac{P^3}{\rho_\nu^2}\frac{\zeta_\nu(A\xi_\nu^2+B\eta_\nu^2+C\zeta_\nu^2)}{\rho_\nu^3} - \frac{5}{2}\frac{P^5}{\rho_\nu^4}\frac{\zeta_\nu(A\xi_\nu^2+B\eta_\nu^2+C\zeta_\nu^2)}{\rho_\nu^3} + \frac{P^5}{\rho_\nu^4}\frac{C\zeta_\nu}{\rho_\nu}\right\}, \end{cases}$$

$\underline{u}_o$

$\underline{u}_\nu$

d: Distance between two particles

P: The radius of the particle

d >> P

No interaction between two particles

$\underline{u}_\nu$:The disturbance due to one particle

$\underline{u}_o$:the velocity of the pure fluid

$\underline{u}(x,y,z) = \underline{u}_o + \Sigma\underline{u}_\nu)$

$$W = 2\delta^2 k + n\delta^2 k\Phi,$$

or

(7b)

$$W = 2\delta^2 k\left(1 + \frac{\phi}{2}\right),$$

n: # of particles per volume fluid

Φ: volume of one particle

the principal dilatations of the mixture

$$u = Ax + \sum u_v$$
$$v = By + \sum v_v$$
$$w = Az + \sum w_v$$

$$A^* = (\frac{\partial u}{\partial x})_{x=0} = A + \sum(\frac{\partial u_\upsilon}{\partial x})_{x=0} = A - \sum(\frac{\partial u_\upsilon}{\partial x_\upsilon})_{x=0}$$
$$B^* = (\frac{\partial v}{\partial y})_{y=0} = B + \sum(\frac{\partial v_\upsilon}{\partial y})_{y=0} = B - \sum(\frac{\partial v_\upsilon}{\partial y_\upsilon})_{y=0}$$
$$C^* = (\frac{\partial w}{\partial z})_{z=0} = C + \sum(\frac{\partial w_\upsilon}{\partial z})_{z=0} = C - \sum(\frac{\partial w_\upsilon}{\partial z_\upsilon})_{z=0}$$

Divergence theorem

$$A^* = A - n\int \frac{\partial u_\upsilon}{\partial x_\upsilon} dV = A - n\int \frac{u_\upsilon x_v}{r_v} ds \qquad (\frac{\partial u_\upsilon}{\partial y_\upsilon} = \frac{\partial u_\upsilon}{\partial z_\upsilon} = 0)$$
$$B^* = B - n\int \frac{\partial v_\upsilon}{\partial y_\upsilon} dV = B - n\int \frac{v_\upsilon y_v}{r_v} ds \qquad (\frac{\partial v_\upsilon}{\partial x_\upsilon} = \frac{\partial v_\upsilon}{\partial z_\upsilon} = 0)$$
$$C^* = C - n\int \frac{\partial w_\upsilon}{\partial x_\upsilon} dV = C - n\int \frac{w_\upsilon z_v}{r_v} ds \qquad (\frac{\partial w_\upsilon}{\partial x_\upsilon} = \frac{\partial w_\upsilon}{\partial y_\upsilon} = 0)$$

Principal dilatations

$$A^* = A(1-\phi)$$
$$B^* = B(1-\phi)$$
$$C^* = C(1-\phi)$$

$$\delta^{*2} = A^{*2} + B^{*2} + C^{*2} = \delta^2(1-2\phi)$$

Viscosity of the mixture

* : mixture

$$W^* = 2\delta^2 k\left(1+\frac{\phi}{2}\right)$$

$$W^* = 2\delta^{*2} k^*$$

Volume fraction of particles

$$k^* = k\frac{1+\frac{\phi}{2}}{1-2\phi} \approx k\left(1+\frac{\phi}{2}\right)(1+2\phi) \approx k\left(1+\frac{5}{2}\phi+O(\phi^2)\right) \qquad \phi<2\%$$

Viscosity of the mixture

Viscosity of the pure fluid

The rheology of concentrated suspensions[1]

- Viscosity does not obey Einstein's formula
- Normal stress
- Particles migrate
- Stress does not reach steady state instantaneously

… …

[1] Andreas Acrivos, *The rheology of concentrated suspensions: latest variations on a theme by Albert Einstein*, Indo-US Joint Conference'04, Mumbai, Indian, 2004

An application: from viscosity and diffusion coefficients to Avogadro number

ω: velocity; N: Avogadro number;
D: diffusion coefficient; ρ: density
m: molecular weight; K: drag force

Stokes's law

$$\omega = \frac{K}{6\pi kP} \quad \Rightarrow \quad D = \frac{RT}{6\pi k} \cdot \frac{1}{NP} \quad \Rightarrow \quad \boxed{NP = \frac{RT}{6\pi k}\frac{1}{D}}$$

$$\frac{k^*}{k} = 1 + \frac{5}{2}\phi = 1 + \frac{5}{2}n\frac{4}{3}\pi P^3$$

$$\frac{n}{N} = \frac{\rho}{m}$$

$$\Rightarrow \quad \boxed{NP^3 = \frac{3}{10\pi}\frac{m}{\rho}\left(\frac{k^*}{k} - 1\right)}$$