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

Fang Xu

June 11\textsuperscript{th} 2007
Hatsopoulos Microfluids Laboratory
Department of Mechanical Engineering
Massachusetts Institute of Technology
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


• In the presence of one particle
  1) velocity profile
  2) the rate of dissipation of mechanical energy
• In the presence of 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

(No body torque) 

(x, y, z) 

(x₀, y₀, z₀) 

Incompressibility

\[ \nabla u + (\nabla u)^T = \frac{1}{2} \begin{bmatrix} A & 0 & 0 \\ 0 & B & 0 \\ 0 & 0 & C \end{bmatrix} \]

\[ \bar{u} = [u_0 \ v_0 \ w_0] \]

\[ x - x_0 = \xi \quad u_0 = A \xi \]
\[ y - y_0 = \eta \quad v_0 = B \eta \]
\[ z - z_0 = \zeta \quad w_0 = C \zeta \]

\[ \nabla \cdot \bar{u} = A + B + C = 0 \]
Governing equations and boundary conditions for the flow past a sphere

Navier-Stokes equation: \( k: \) viscosity of the fluid

\[
\rho \left[ \frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} \right] = \rho \mathbf{g} - \nabla p + k \nabla^2 \mathbf{u}
\]

Steady state \ No inertia \ Neglect gravity

\[
\nabla p = k \nabla^2 \mathbf{u} \quad \text{(Stokes equations)}
\]

\[
\nabla \cdot \mathbf{u} = 0 \quad \text{(Incompressibility)}
\]

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

B.C. \( u = v = w = 0 \) at the surface of the sphere
To find solutions (1)

Velocity without the presence of the particle

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

disturbance due to the particle

\[ x - x_0 = \xi \]
\[ y - y_0 = \eta \]
\[ z - z_0 = \zeta \]

\( (x, y, z) \)

\( (x_0, y_0, z_0) \)

\( u_1 \to 0 \)

\( v_1 \to 0 \quad as \ \rho \to \infty, \quad \rho = \sqrt{\xi^2 + \eta^2 + \zeta^2} \)

\( w_1 \to 0 \)
To find solutions (2)

The structure of $u$:

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

Harmonic functions

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

Which satisfies the governing equations

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

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

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

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

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

$$\nabla \cdot u = 0$$
To find solutions (3)

Governing equations

Harmonic function

\[ \nabla^2 p = \nabla \cdot \nabla p = \nabla \cdot (k \nabla^2 u) = k \nabla^2 (\nabla \cdot u) = 0 \]

\[ \frac{p}{k} = 2c \frac{\rho}{\partial \xi^2} \]

\[ V = c \frac{\partial^2 \rho}{\partial \xi^2} + b \frac{\rho}{\partial \xi^2} + a \frac{\xi^2 - \eta^2}{2} \]

\[ \partial \frac{1}{\partial \xi^2} \]

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

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

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

\[ \frac{\partial^2 \frac{1}{\rho}}{\partial \zeta^2} = \frac{3\zeta^2}{\rho^5} - \frac{1}{\rho^3} \]
solutions for flow past a sphere

\[
\dot{\rho} = - \frac{5}{3} k P^3 \left\{ A \frac{\partial^2 (I)}{\partial \xi^2} + B \frac{\partial^2 (I)}{\partial \eta^2} \right\} + \text{const.}
\]

\[
p = p' + \text{const.} + \frac{\partial^2 (I)}{\partial \xi^2} + \text{const.}
\]

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

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

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

\[
u_1 \to 0
\]

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

\[
w_1 \to 0
\]
The rate of dissipation of mechanical energy

\[ W = \int ([t(n) \cdot u] ds = \int (n \cdot t) \cdot u ds \]

\[ t = -pI + 2kE \]

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

(P 46-48)

Neglect higher order terms

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

where we put

\[ \delta^2 = A^2 + B^2 + C^2, \]

\[ \frac{4\pi}{3} R^3 = V \text{ and } \frac{4\pi}{3} P^3 = \Phi \]
With the presence of multiple particles

\[ u(x, y, z) = u_0 + \sum u_v \]

- \( u_0 \): the velocity of the pure fluid
- \( u_v \): the disturbance due to one particle

**Equations:**

\[
\begin{align*}
\xi_v &= x - x_v \\
\eta_v &= y - y_v \\
\zeta_v &= z - z_v
\end{align*}
\]

- \( d \): Distance between two particles
- \( P \): The radius of the particle
- \( d >> P \)
- No interaction between two particles

**Other Variables:**

- \( n \): # of particles per volume fluid
- \( \Phi \): volume of one particle

\[ W = 2\delta^2 \kappa + n\delta^2 k\Phi, \]

or

\[ W = 2\delta^2 \kappa \left( 1 + \Phi / 2 \right), \]
The principal dilatations of the mixture

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

\[ A^* = (\frac{\partial u}{\partial x})_{x=0} = A + \sum (\frac{\partial u_v}{\partial x})_{x=0} = A - \sum (\frac{\partial u_v}{\partial x})_{x=0} \]
\[ B^* = (\frac{\partial v}{\partial y})_{y=0} = B + \sum (\frac{\partial v_v}{\partial y})_{y=0} = B - \sum (\frac{\partial v_v}{\partial y})_{y=0} \]
\[ C^* = (\frac{\partial w}{\partial z})_{z=0} = C + \sum (\frac{\partial w_v}{\partial z})_{z=0} = C - \sum (\frac{\partial w_v}{\partial z})_{z=0} \]

**Divergence theorem**

\[ A^* = A - n \int \frac{\partial u_v}{\partial x_v} dV = A - n \int \frac{u_v x_v}{r_v} ds \]
\[ B^* = B - n \int \frac{\partial v_v}{\partial y_v} dV = B - n \int \frac{v_v y_v}{r_v} ds \]
\[ C^* = C - n \int \frac{\partial w_v}{\partial z_v} dV = C - n \int \frac{w_v z_v}{r_v} ds \]

\[ \frac{\partial u_v}{\partial y_v} = \frac{\partial u_v}{\partial z_v} = 0 \]
\[ \frac{\partial v_v}{\partial x_v} = \frac{\partial v_v}{\partial z_v} = 0 \]
\[ \frac{\partial w_v}{\partial x_v} = \frac{\partial w_v}{\partial y_v} = 0 \]

**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

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

\[ W^* = 2\delta^2 k^* \]

Volume fraction of particles

\[ k^* = k \frac{1 + \frac{\phi}{2}}{1 - 2\phi} \approx k(1 + \frac{\phi}{2}) (1 + 2\phi) \approx k(1 + \frac{5}{2} \phi + O(\phi^2)) \quad \phi < 2\%
\]

Viscosity of the mixture

Viscosity of the pure fluid
• Viscosity does not obey Einstein’s formula
• Normal stress
• Particles migrate
• Stress does not reach steady state instantaneously

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

\[ \omega = \frac{K}{6\pi kP} \quad D = \frac{RT}{6\pi k} \cdot \frac{1}{NP} \quad NP = \frac{RT}{6\pi kD} \]

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

\[ \frac{n}{N} = \frac{\rho}{m} \]

\[ NP^3 = \frac{3}{10\pi} \frac{m}{\rho} \left( \frac{k^*}{k} - 1 \right) \]