1905-2005

www.aip.org/history/einstein/

- Twenty-six year old patent clerk in Bern, Switzerland
- Wrote FIVE major physics papers:
  1. Photo-electric effect (Nobel Prize 1921)
  2. Doctoral dissertation
  3. Brownian motion
  4. Special relativity
  5. Special relativity (addendum)

World Year of
PHYSICS
2005

www.physics2005.org

Europe in 1900

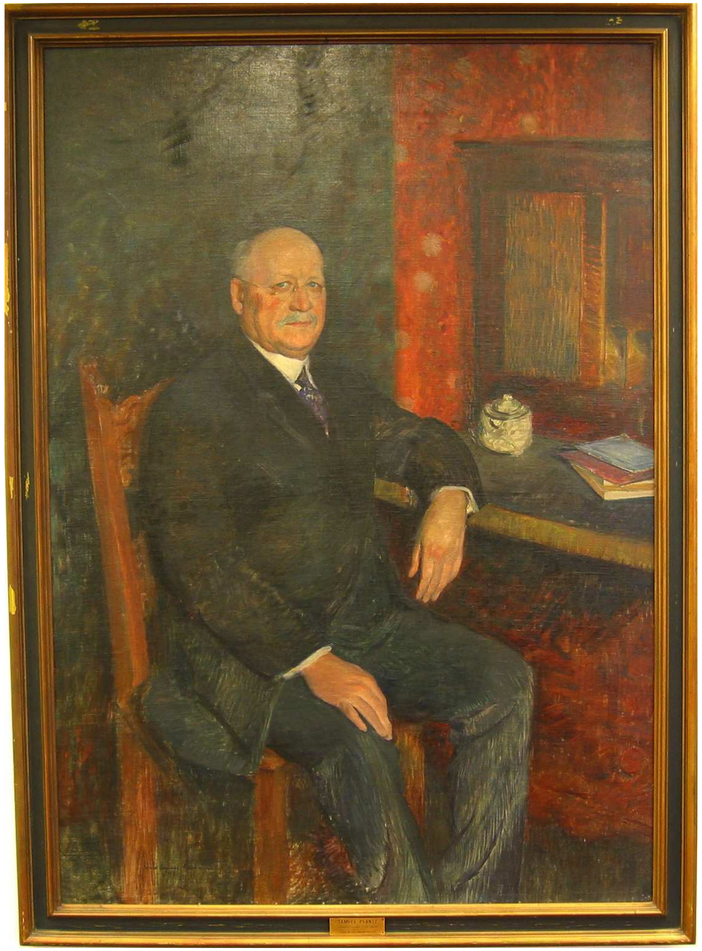
© www.euratlas.com

1905 Presidents

Theodore Roosevelt,
President of U.S.

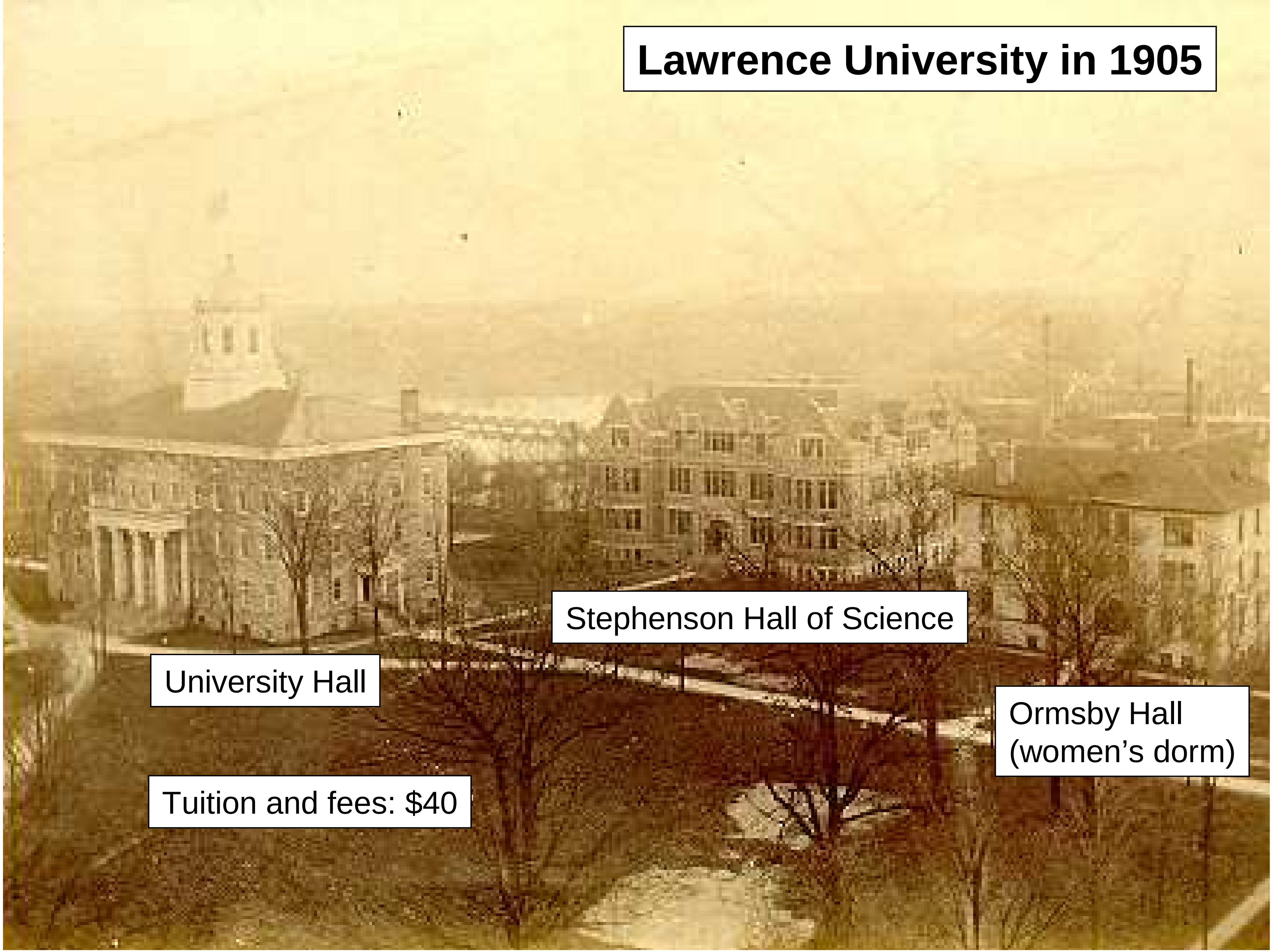
www.fadedgiant.net

Samuel Plantz, President of
Lawrence University



www.lawrence.edu/library

Lawrence University in 1905



Stephenson Hall of Science

University Hall

Ormsby Hall
(women's dorm)

Tuition and fees: $40

Physics and Astronomy at Lawrence in 1905

Faculty:

- **Charles Watson Treat** A.M., Vice President and Philetus Sawyer Professor of Physics
- **Perry Wilson Jenkins**, A.M., Professor of Mathematics and Astronomy, and Director of the Underwood Observatory
- **John Charles Lymer**, A.M., S.T.B., Acting Professor of Mathematics and Director of the Underwood Observatory

Courses:

- General Astronomy
- Practical Astronomy
- Meteorology
- Laboratory Course
- General Physics (Mechanics of Solids and Fluids)
- General Physics (Sound and Light)
- General Physics (Heat, Electricity, and Magnetism)
- Advanced Laboratory Course
- Applied Electricity
- Optics
- Special Work

Underwood Observatory

Einstein’s 1905 Paper on Brownian Motion

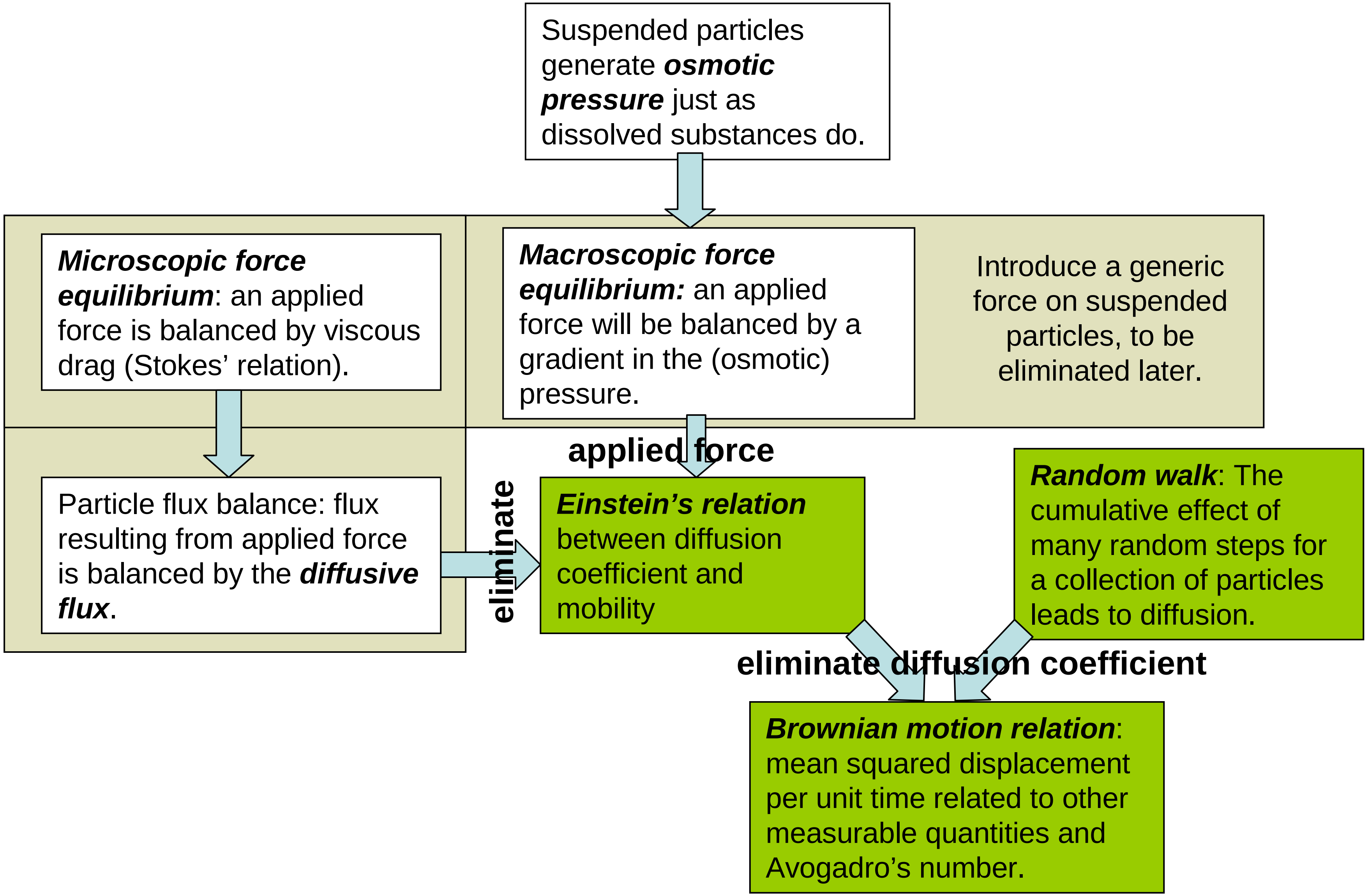
Über die von der molekularkinetischen Theorie der Wärme geforderte Bewegung von in ruhenden Flüssigkeiten suspendierten Teilchen

Annalen der Physik **17**, 549 (1905)

On the Movement of Small Particles Suspended in Stationary Liquids Required by the Molecular-Kinetic Theory of Heat

Matthew R. Stoneking
Physics Colloquium
Lawrence University
20 January 2005

Map of Einstein’s Paper



Suspended particles generate ***osmotic pressure*** just as dissolved substances do.

Microscopic force equilibrium: an applied force is balanced by viscous drag (Stokes’ relation).

Macroscopic force equilibrium: an applied force will be balanced by a gradient in the (osmotic) pressure.

Introduce a generic force on suspended particles, to be eliminated later.

applied force

Particle flux balance: flux resulting from applied force is balanced by the ***diffusive flux***.

eliminate

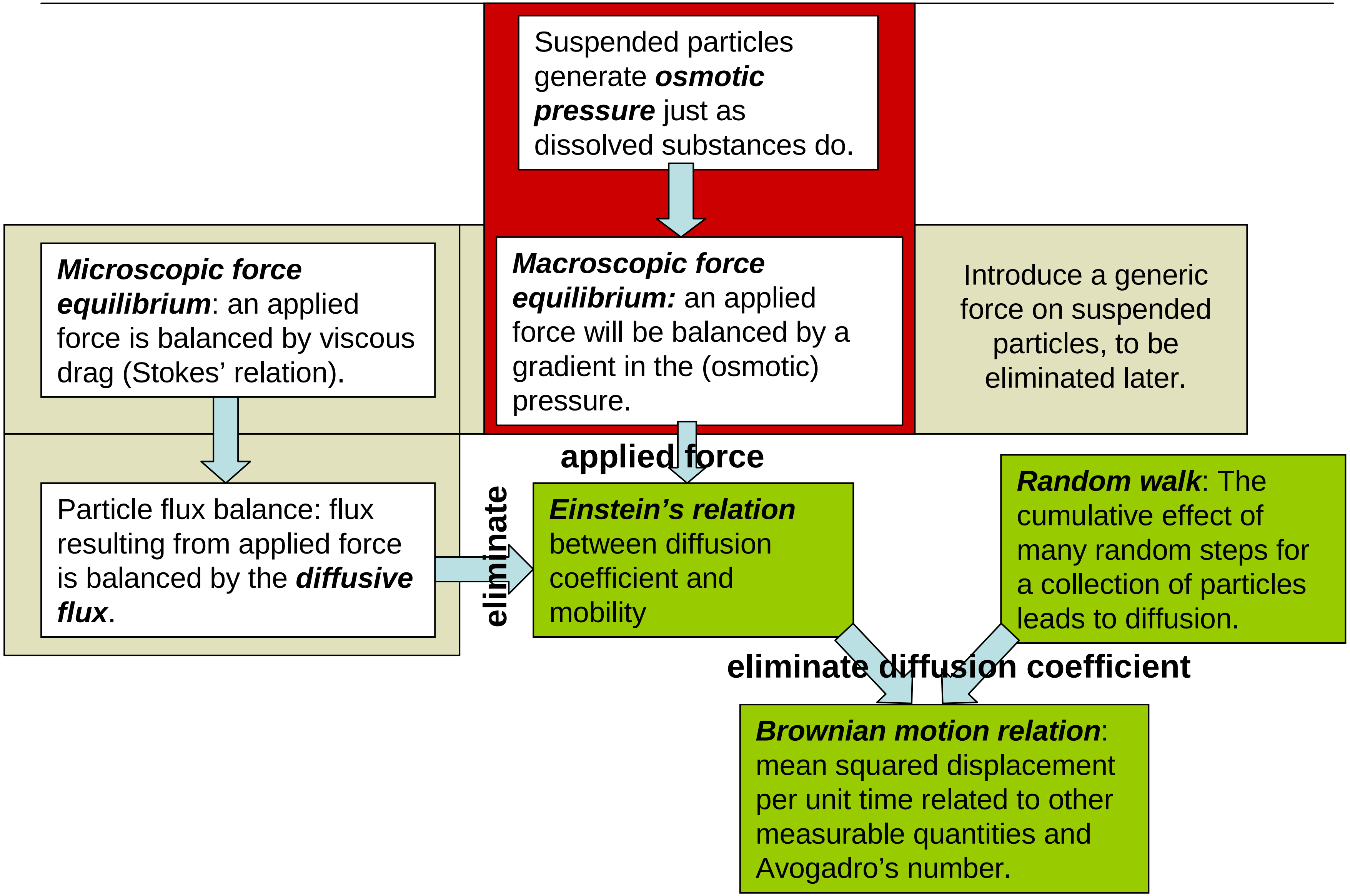
Einstein’s relation between diffusion coefficient and mobility

Random walk: The cumulative effect of many random steps for a collection of particles leads to diffusion.

eliminate diffusion coefficient

Brownian motion relation: mean squared displacement per unit time related to other measurable quantities and Avogadro’s number.

Map of Einstein’s Paper



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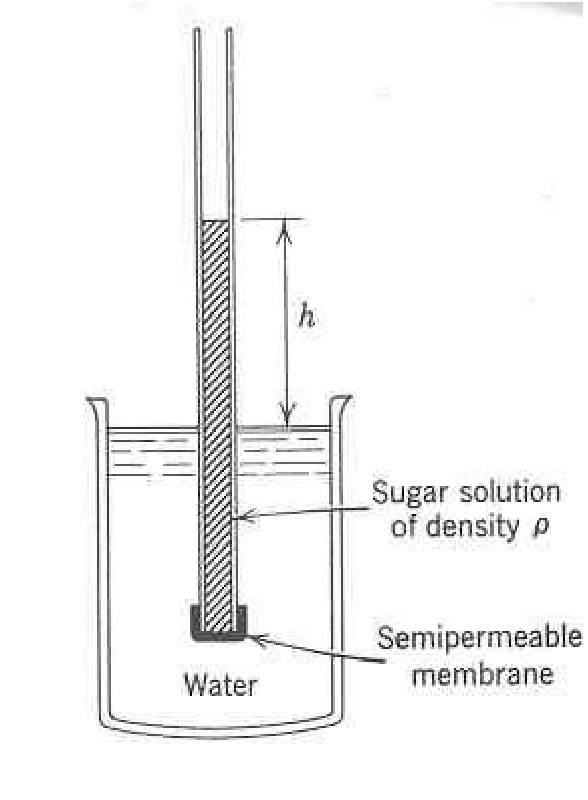
Osmotic Pressure (dilute solutions)



$$p_{osmotic}V_{solute} = \frac{N_{solute}}{N_A}RT$$

Einstein's notation: $pV^* = zRT$

The additional pressure exerted by the solute is the same as if the solute were an ideal gas with no solvent present!

van't Hoff's Law (Nobel prize, chemistry 1901)

Recall that 12 g of C contains N_A atoms by definition.

One of the main results of Einstein's paper was to suggest an experimental method for determining Avogadro's number.

Suspensions vs. Solutions

Einstein argued that,
"…from the standpoint of the molecular-kinetic theory of heat … a dissolved molecule differs from a suspended body in size *alone*, and it is difficult to see why suspended bodies should not produce the same osmotic pressure as an equal number of dissolved molecules."

$$p_{osmotic} V_{suspended} = \frac{N_{suspended}}{N_A} RT$$

OR

$$p_{osmotic} = \frac{n_{suspended}}{N_A} RT$$

Einstein's notation: $p = \frac{RT}{N} \frac{n}{V^*} = \frac{RT}{N} \nu$

and, "We will have to assume that the suspended bodies perform an irregular, even though very slow, motion in the liquid due to the liquid's molecular motion." → Kinetic Theory… equipartition theorem

Macroscopic Force Balance

- Consider an external force that acts on only the suspended (or dissolved) bodies.
- In a finite sized vessel, macroscopic equilibrium will be achieved by a balance between the applied force (per unit volume) and the gradient in the osmotic pressure:

$$n_{suspended} F_{applied} = \frac{\partial p_{osmotic}}{\partial x}$$

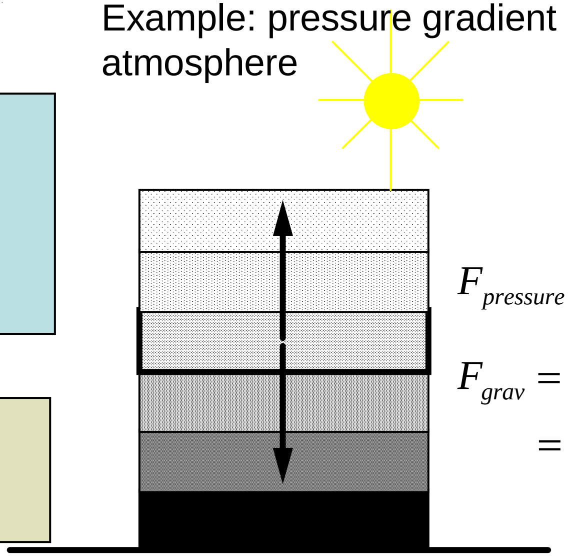
- The gradient of a pressure is a force per unit volume

OR

$$n_{suspended} F_{applied} = \frac{RT}{N_A} \frac{\partial n_{suspended}}{\partial x} \tag{1}$$

Einstein's notation: $\nu K = \frac{RT}{N} \frac{\partial \nu}{\partial x}$

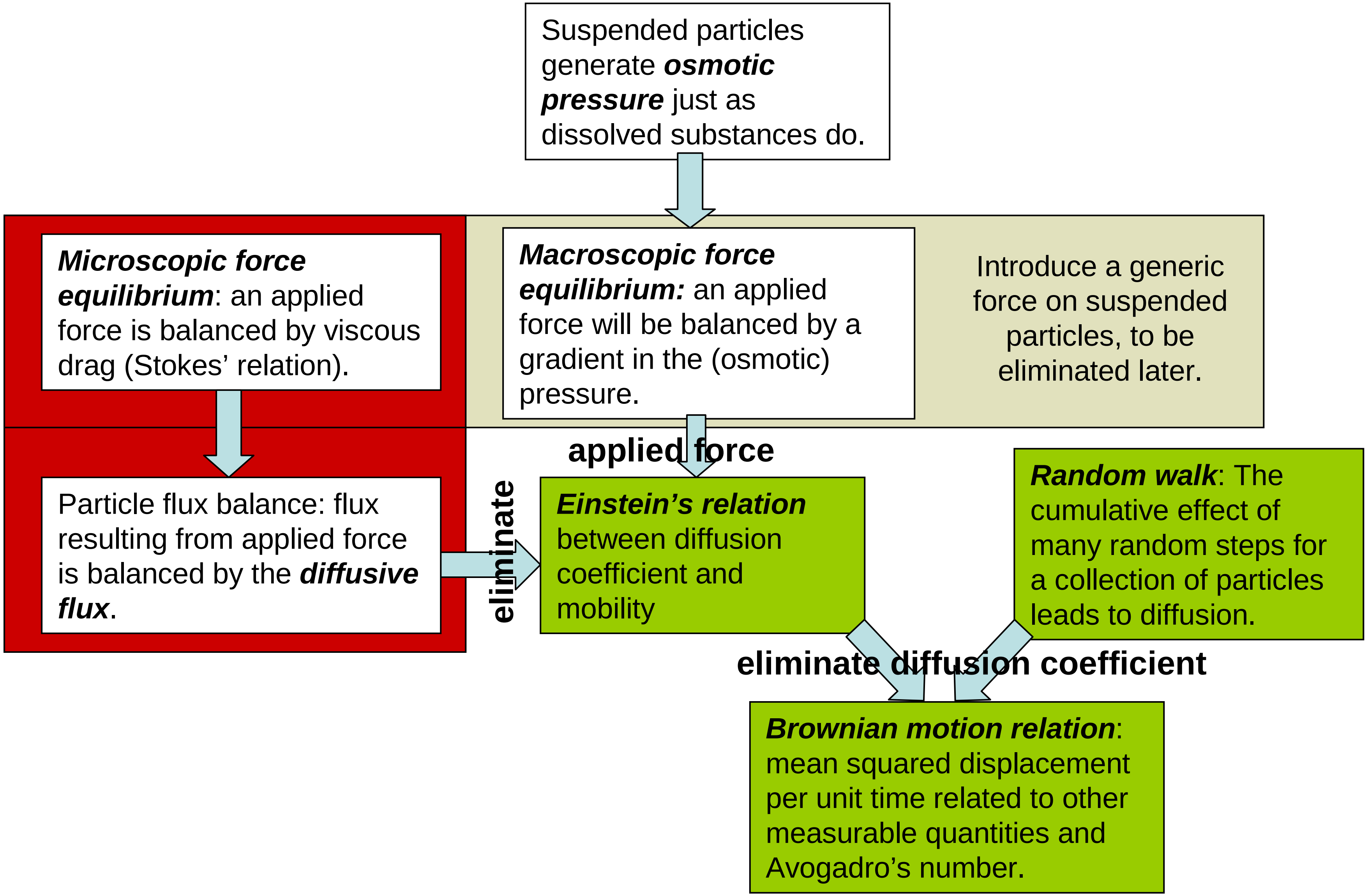
Example: pressure gradient in earth's atmosphere



$$F_{pressure} = -\nabla p \, \Delta V$$

$$F_{grav} = -n(mg)\Delta V$$
$$= -nF_{applied} \, \Delta V$$

Map of Einstein’s Paper



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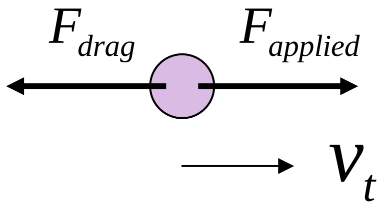
Microscopic Force Balance and Viscous Drag

- Consider the forces on a single suspended particle.
- The presence of the solvent (treated as a continuous fluid) exerts a drag.
- In equilibrium (once terminal velocity is achieved), the applied force and the drag balance each other.



$$F_{applied} = F_{drag}$$

- A low velocities, the drag force (and hence the applied force in equilibrium) is proportional to the velocity.

$$v_t = \mu F_{applied}$$

“mobility”

- Stokes’ relation for a spherical particle moving through a viscous fluid:

$$F_{drag} = 6\pi\eta a v_t$$

viscosity

particle radius

OR, the mobility due to viscous drag is

$$\mu = \frac{1}{6\pi\eta a}$$

Millikan Oil Drop Expt. (1909ff)

Particle Conservation or Flux Balance

- The applied force results in a “flux” of suspended (or dissolved) particles:

(Flux=number of particles passing through a unit area per unit time)

$$\Gamma = n_{suspended} v_t = n_{suspended} \mu F_{applied}$$

- If the fluid is contained in a vessel, the flux will result in a concentration gradient.
- Diffusion is the process that attempts to relax concentration (or density) gradients.
- The “diffusive flux” is given by Fick’s Law:

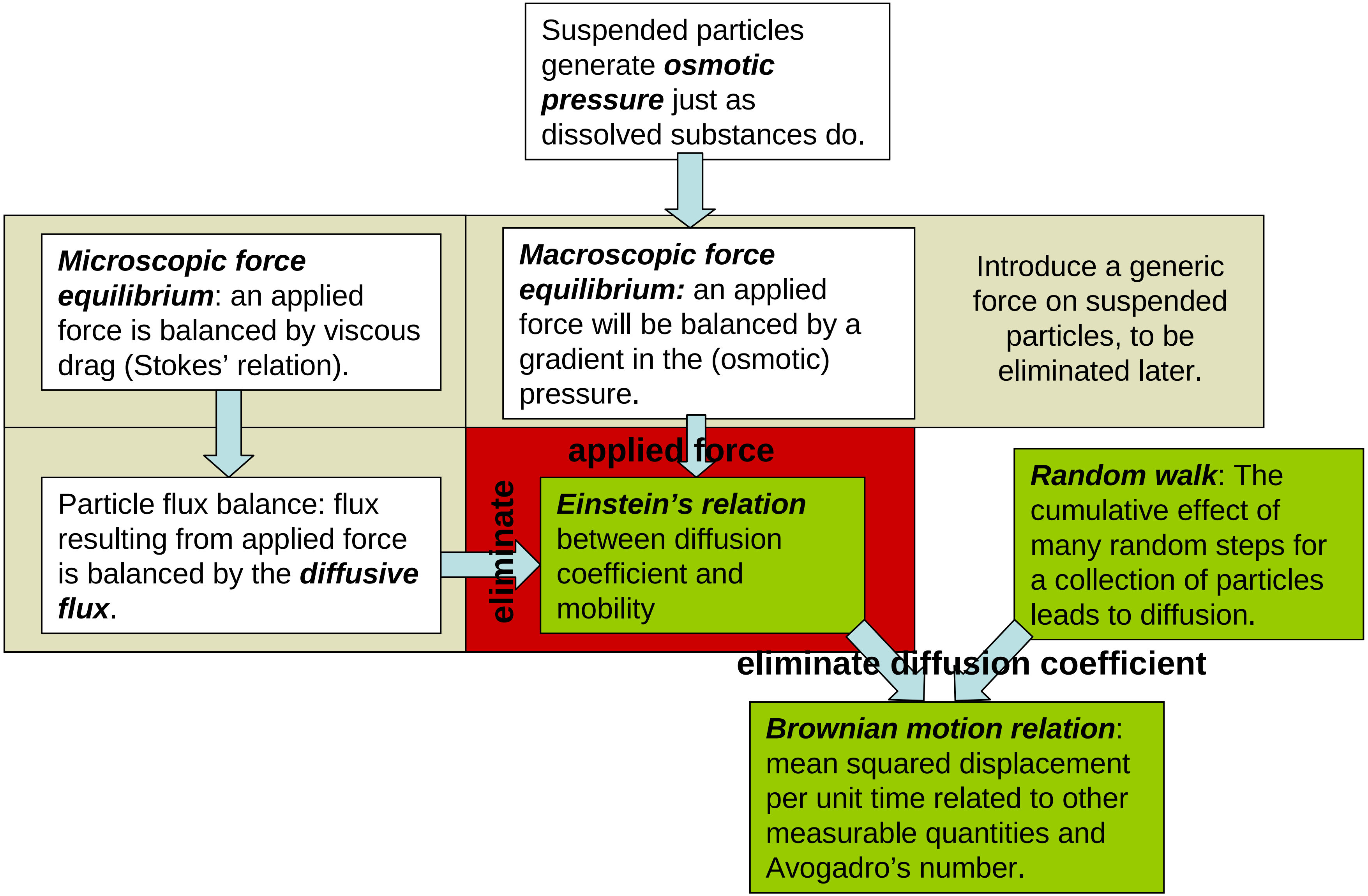
$$\Gamma = D \frac{\partial n_{suspended}}{\partial x}$$

diffusion coefficient

- In equilibrium, the flux due to the applied force, and the diffusive flux will be equal in magnitude

$$n_{suspended} \mu F_{applied} = D \frac{\partial n_{suspended}}{\partial x}$$

Map of Einstein’s Paper



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Einstein’s Relation

- Using Stokes’ relation:

$$(2)\quad \frac{n_{suspended}F_{applied}}{6\pi\eta a} = D\frac{\partial n_{suspended}}{\partial x}$$

$$\frac{\nu K}{6\pi kP} = D\frac{\partial \nu}{\partial x}$$

- Recall Eq. 1: $$n_{suspended}F_{applied} = \frac{RT}{N_A}\frac{\partial n_{suspended}}{\partial x}$$

- Eliminate the applied force from (1) and (2), notice that the concentration gradient falls out. Solve for the diffusion coefficient:

IMPORTANT RESULT #1

$$D = \frac{RT}{N_A}\frac{1}{6\pi\eta a}$$

$$D = \frac{RT}{N}\frac{1}{6\pi kP}$$

Sutherland 1905

More generally:

$$D = \mu\frac{RT}{N_A} = \mu k_B T$$

Einstein’s relation

Used in fluid mechanics, plasma physics, condensed matter physics, biophysics…

A Digression on Einstein’s Doctoral Thesis

- In his doctoral thesis, completed just 11 days before the Brownian motion paper, Einstein used this same relation for molecules dissolved in a solvent:

$$D = \frac{RT}{N_A} \frac{1}{6\pi\eta a}$$

- He obtained a second relationship between N_A and *a* by considering the change in the viscosity when the solute is added to the solvent:

1905 dissertation:

$$\eta^* = \eta \left(1 + \frac{N_A \rho_{solute}}{m_{solute}} \frac{4\pi a^3}{3} \right)$$

↳ $N_A = 2.1 \cdot 10^{23}$

With improved data (1906): $N_A = 4.15 \cdot 10^{23}$

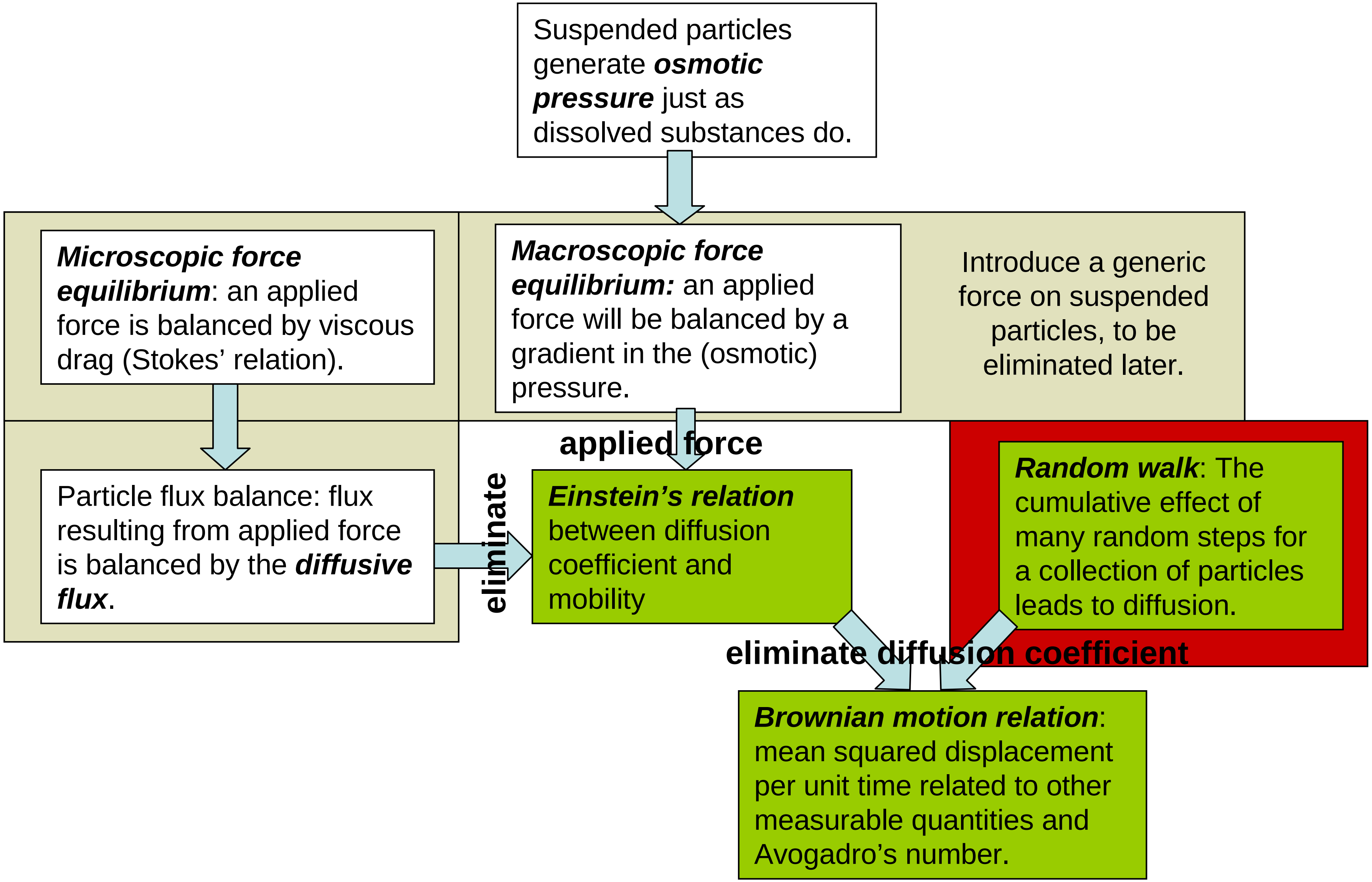
1911 correction:

$$\eta^* = \eta \left(1 + \frac{5}{2} \frac{N_A \rho_{solute}}{m_{solute}} \frac{4\pi a^3}{3} \right)$$

↳ $N_A = 6.6 \cdot 10^{23}$

Also get radius of solute molecules (assumed spherical)
Title of dissertation: “A New Determination of Molecular Dimensions”

Map of Einstein's Paper



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Diffusion of Suspended Particles

- In his doctoral thesis, Einstein relied on measurements of the diffusion of a solute through a solvent (and on changes in the solvent's viscosity).

- In this paper, he considered whether the diffusion might be directly observed under a microscope via the motion of individual *suspended* particles.

- Einstein and Smoluchowski, concurrently, were the first to make a quantitative connection between a random walk process and diffusion.

- "It is possible that the motions to be discussed here are identical with the so-called 'Brownian molecular motion'; however, the data available to me on the latter are so imprecise that I could not for a definite opinion on this matter."

Brownian Motion

- 1827: Botanist, Robert Brown, observes “swarming” motion of plant pollen suspended in still water… determines that it is NOT due to motion of living beings.

- 1860s: Conjecture that Brownian motion is due to the internal motions of the fluid (Cantoni, Delsaulx, Carbonelle, and Gouy), but cannot be due to individual collisions with solvent molecules (von Naegeli and Ramsey).

- 1900 (Poincare) “One would believe [we are] seeing Maxwell’s demons at work”

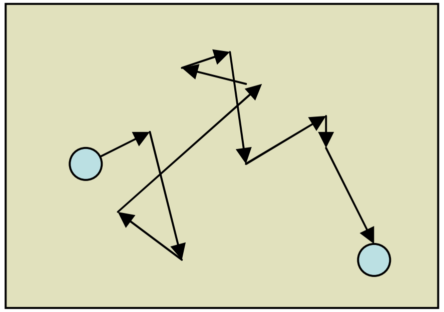
- 1904 (Poincare) “We see under our eyes now motion transformed into heat by friction, now heat changed inversely into motion. This is the contrary of Carnot’s principle.”

- 1905 (Einstein) “If it is really possible to observe the motion to be discussed here, along with the laws it is expected to obey, then classical thermodynamics can no longer be viewed as strictly valid even for microscopically distinguishable spaces…”

Reference: “Subtle is the Lord…the Science and the Life of Albert Einstein”, by Abraham Pais.

Random Walk ⇨ Diffusion

- Take a particle, initially at the origin.
- Every time step, the particle takes a step to the right or the left with equal probability.



Time	x	$\langle x \rangle$	$\langle x^2 \rangle$
0	$x_o = 0$	0	$\langle x_o{}^2 \rangle = 0$
τ	$x_1 = \pm\Delta$	0	$\langle x_1{}^2 \rangle = \Delta^2$
2τ	$x_2 = x_1 \pm \Delta$	0	$\langle x_2{}^2 \rangle = \langle (x_1 \pm \Delta)^2 \rangle = \langle x_1{}^2 \rangle \pm 2\Delta \langle x_1 \rangle + \Delta^2 = 2\Delta^2$
3τ	$x_3 = x_2 \pm \Delta$	0	$\langle x_3{}^2 \rangle = \langle (x_2 \pm \Delta)^2 \rangle = \langle x_2{}^2 \rangle \pm 2\Delta \langle x_2 \rangle + \Delta^2 = 3\Delta^2$
4τ	$x_4 = x_3 \pm \Delta$	0	$\langle x_4{}^2 \rangle = \langle (x_3 \pm \Delta)^2 \rangle = \langle x_3{}^2 \rangle \pm 2\Delta \langle x_3 \rangle + \Delta^2 = 4\Delta^2$

$$\boxed{\langle x^2 \rangle = \left(\frac{\Delta^2}{\tau} \right) t}$$

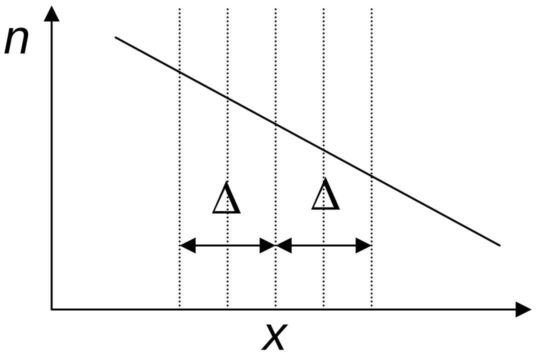
"Naegeli believes that [the effect] of collisions should in the average cancel each other …This is the same conceptual error as when a gambler would believe that he can never lose a larger amount than a single stake."
– M.R. von Smolan-Smoluchoswki
A. Pais, "Subtle is the Lord;" The Science and the Life of Albert Einstein

Random Walk ⇨ Diffusion

- Consider the flux of particles due to *independent* random walks, in the presence of a density gradient.
- In one time step, the net flux of particles past a point is $\Gamma = \frac{N_+ - N_-}{A\tau}$

where $\frac{N_+}{A} = \frac{1}{2} n\left(x - \frac{\Delta}{2}\right)\Delta$ and $\frac{N_-}{A} = \frac{1}{2} n\left(x + \frac{\Delta}{2}\right)\Delta$

$$\Gamma = \frac{1}{2}\frac{\Delta}{\tau}\left[n\left(x+\frac{\Delta}{2}\right) - n\left(x-\frac{\Delta}{2}\right)\right] = \frac{\Delta^2}{2\tau}\frac{\partial n}{\partial x}$$



- Compare to Fick's Law: $\Gamma = D\frac{\partial n}{\partial x}$

- Connection between single particle random walk and diffusion:

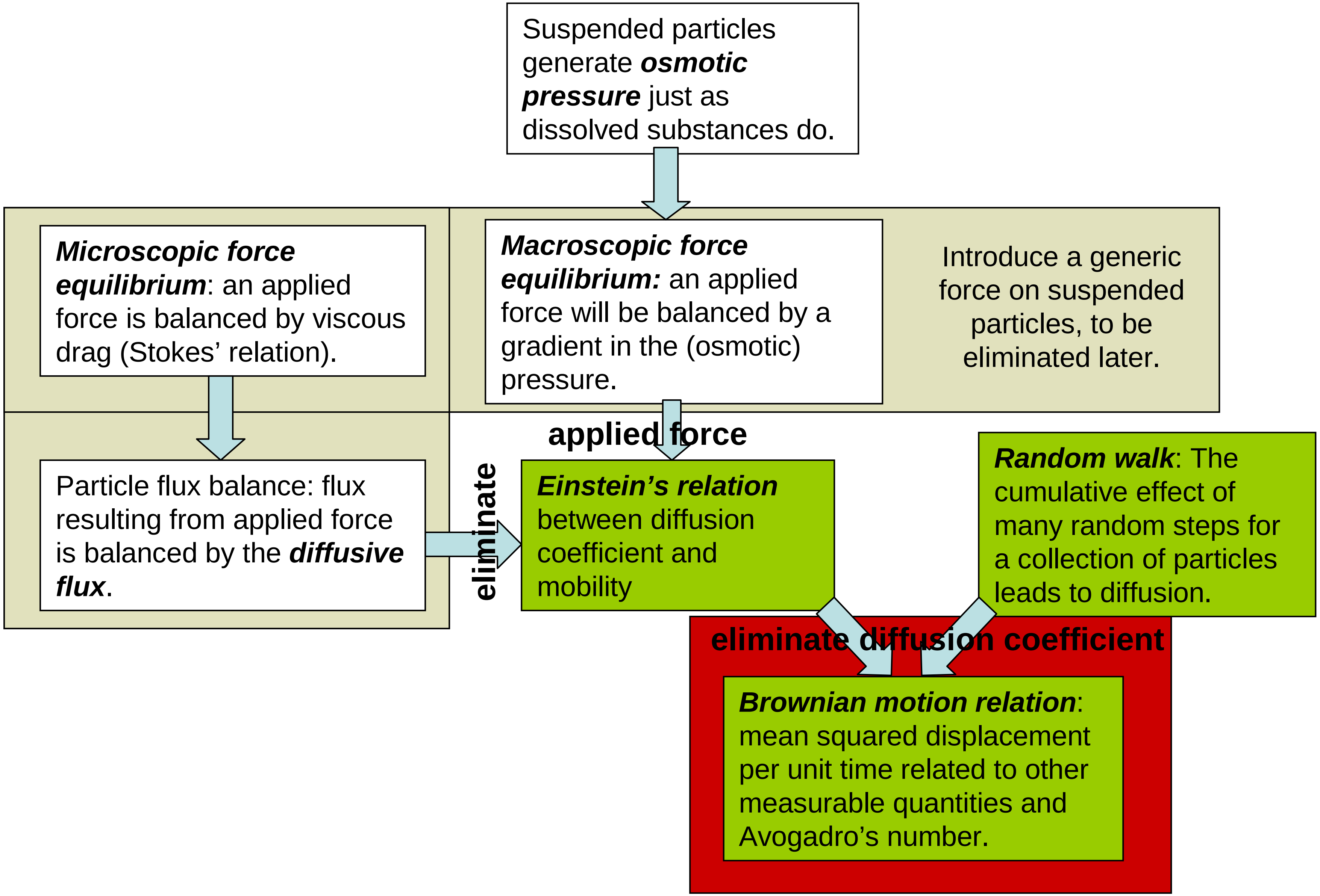
IMPORTANT RESULT #2

$$D = \frac{\Delta^2}{2\tau} = \frac{\langle x^2 \rangle}{2t}$$

Smoluchowski (1906)

$$D = \frac{1}{2\tau}\int_{-\infty}^{+\infty} \Delta^2 \varphi(\Delta) d\Delta$$

Map of Einstein’s Paper



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Observations of Brownian Motion can be used to Measure Avogadro’s Number

- Einstein performed a more general analysis with a distribution of step sizes and obtained the same result,

$$\left\langle x^2 \right\rangle = 2Dt$$

$$\lambda_x = \sqrt{2Dt}$$

- Recall from the Einstein relation: $D = \frac{RT}{N_A} \frac{1}{6\pi\eta a}$

  - Eliminate *D*:

$$\left\langle x^2 \right\rangle = \frac{RT}{N_A} \frac{t}{3\pi\eta a}$$

OR

IMPORTANT RESULT #3

$$N_A = \frac{RT}{\left\langle x^2 \right\rangle} \frac{t}{3\pi\eta a}$$

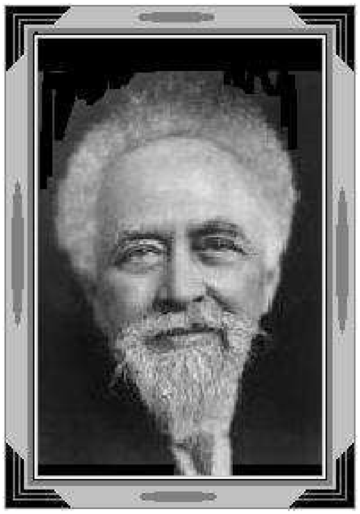
$$N = \frac{RT}{\lambda_x{}^2} \frac{t}{3\pi kP}$$

IMPORTANT RESULT #3

$$N_A = \frac{RT}{\langle x^2 \rangle} \frac{t}{3\pi\eta a}$$

“Let us hope that a researcher will soon succeed in solving the problem posed here, which is of such importance in the theory of heat!”

Jean-Baptiste Perrin used AE’s result to measure N_A and received the Nobel Prize in 1926…”for his work on the discontinuous structure of matter, and especially for his discovery of sedimentation equilibrium.”



www.sobiografias.hpg.ig.com.br/JeanBaPe.html

The Reality of Atoms/Molecules

"…the issue [the reality of atoms and molecules] was settled [in the first decade of the 20th century] once and for all because of the extraordinary agreement in the values of N_A obtained by many methods. … From subjects as diverse as radioactivity, Brownian motion, and the blue of the sky, it was possible to state by 1909, that a dozen independent ways of measuring N_A yielded results all of which lay between 6 and 9 X 10^{23}."
- A. Pais,'Subtle is the Lord', The Science and the Life of Albert Einstein

General Inorganic Chemistry at Lawrence University (1905)

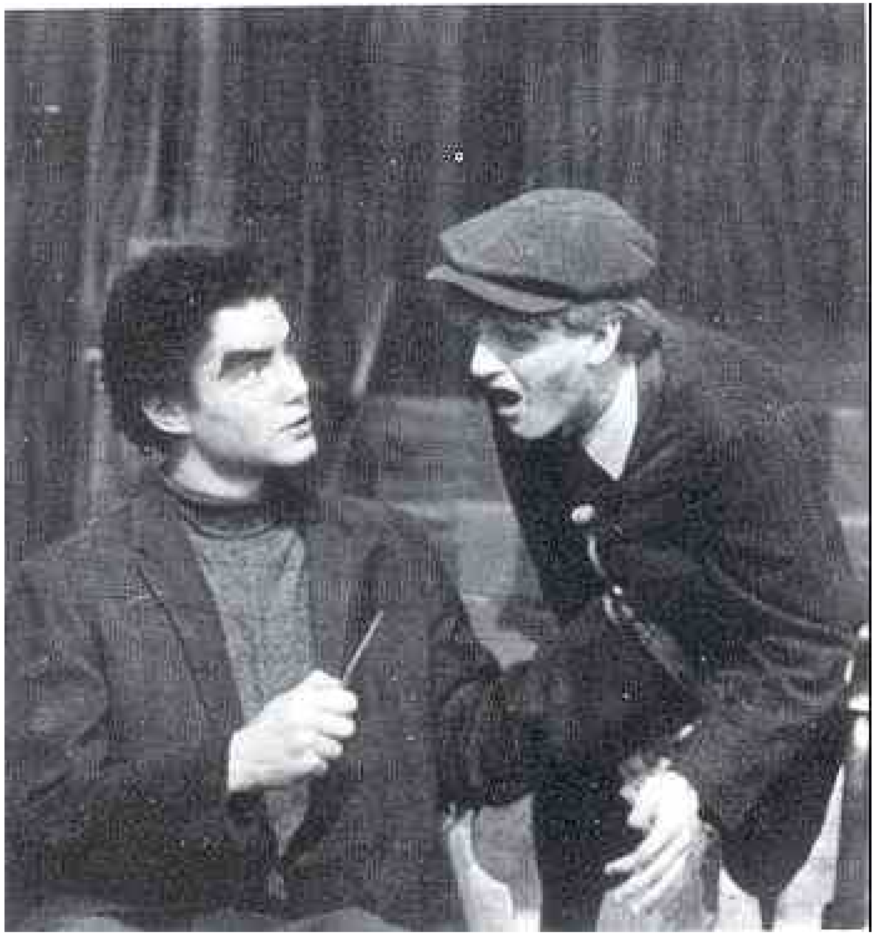
"The first part of the course is devoted to a study of the laws of chemical union, solution, acids, bases, salts, **atoms**, **molecules**, **valency, ionization**, vapor density and the gas laws, **atomic masses**, **molecular formulae**, **chemical equations**, etc. developed quantitatively as far as seems consistent for beginners."

Chemistry faculty:

- Lewis A. Youtz, M.S., Ph. D., Robert McMillan Professor of Chemistry

Eighty years later … 1985

- M. Stoneking plays the role of Einstein
- Dr. Einstein in Irondale H.S. production of ***Arsenic and Old Lace***



Acknowledgments

- Susan Richards … for information on LU physics obtained from the university archives.
- Professor Bart DeStasio … for assistance in obtaining video images of Brownian motion.
- Debbie Roman … for assistance with osmotic pressure demonstration.