

Un viejo amigo, estudiante mexicano en la UNAM hace algunos años, nos envía esta contribución en inglés sobre la historia y la enseñanza del movimiento browniano, ahora que realiza una estancia posdoctoral.

On the Application of Brownian Motion in Teaching Physical Chemistry

*Gerardo Soto-Campos**

Abstract

Some aspects of the theory of transport are elucidated by an stochastic approach; we derive Fick's second law, and discuss the relevant points of the theory of Brownian motion, which allow to determine Avogadro's constant, N_0 . At the end we use the formulation of the paper to estimate N_0 .

Introduction

One of the main purposes of this paper is to introduce students of physical chemistry into the fascinating world of random processes (more generally called stochastic processes). This practice is an attempt to remove the "mental barrier" that time dependent (non-equilibrium) processes are esoteric useless applications of pedantic mathematics. As chemists we study time processes in the traditional courses of chemical kinetics; however, often the time dependence is washed away by integrating empirical rate laws, or making assumptions of equilibrium or formations of long time steady states. Even though these approximations are very useful, it is important to keep in mind that they are only limiting cases.

Since this is an introduction to the subject of non-equilibrium addressed to chemistry majors, I have chosen a topic of high repercussion in chemistry, *Brownian movement*. That is, the random motion that small particles¹ perform when dispersed in a fluid, or a solid.² This type of motion is named after the British naturalist Robert Brown (1828), who was the first scientist to realize that the nature of such motion is physical rather than biological as many of his colleagues thought.

Though an excellent experimentalist, Brown lacked the right theoretical explanation for his observations. Indeed,

brownian motion remained in oblivion for over fifty years until two brilliant young theorists, Einstein (1956) and Smoluchowski (1908), explained it fully. However, the experimental figure behind the phenomenon of brownian motion is the French physicist Perrin. It was Perrin (1908, 1914) who showed the validity of Einstein's theories, and consequently proved univocally the existence of atoms.³ Furthermore, Perrin's experiments give an estimate of the value of Avogadro's constant. In what follows we derive some of Einstein's results from a stochastic point of view. We also discuss some of the results of Einstein's theory and describe the experiments of Perrin. It is shown how these classical studies allow to determine the value of Avogadro's constant. Finally, in the concluding remarks we attempt to connect theory with reality by actually computing Avogadro's number using experimental and theoretical results from the literature. We strongly encourage the curious student to try to follow the derivations by himself or herself.

Einstein's statistical theories

Einstein and Smoluchowsky are the first scientists who explained Brownian motion from a purely physical point of view. In this section, we derive a fundamental equation in the theory of transport from a strictly microscopic point of view. We perform such task starting from a discrete, one dimensional lattice. Then we write a balance for the probability of finding a particle at a given lattice point. One should notice that probability balances are completely equivalent to mass balances. The difference between one another is a multiplicative constant, i.e. the total number of particles diffusing in the liquid.

Figure 1 shows a discrete, one-dimensional lattice. Particles can travel along the sites of the lattice, making one-step jumps, but with complete freedom to move right or left. To keep things simple, we assume that the rates of transition among sites of the lattice are constant. We denote such rates with the letter a .

* Department of Chemistry and Biochemistry, University of California Los Angeles, USA.

Recibido: 20 de febrero de 1997; Aceptado: 15 de abril de 1997.

¹ For example colloidal dispersions of metals; that is, clusters of atoms of a metal enclosed by long molecules with a polar group facing the metal, and a non-polar end sticking out of the cluster.

² Although in this paper we only talk about dispersion in fluids, it is important to mention that the phenomenon of dispersion in solids is fundamental in the study of the storage of nuclear wastes, where radioactive particles can diffuse through the walls of their containers.

³ Perrin's experiments destroyed the old school of thought that atoms are mere mental artifacts to explain cleverly some experimental observations. This old school was lead by the eminent French physicist Duhem and the equally famous German physical chemist Ostwald.

⁴ In a discrete time random balance of probability, particles *always* jump

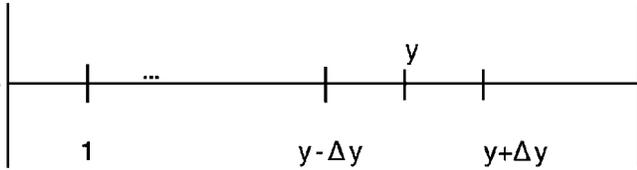


Figure 1. Discrete one-dimensional lattice.

Balances of probability

To study the balance of probability, we take time as a continuous variable. One could take it as a discrete one, but the analysis in such case gets messier. Furthermore, in the limit of our interest both balances are entirely equivalent. Let the time for a transition be the infinitesimal quantity dt . The probability of a transition between adjacent sites is the product

$$a dt$$

Figure 2 shows any three adjacent sites of the lattice. Notice that particles can never be located in between sites of the lattice. The question one wishes to answer is what the probability of finding a particle on site y at a time $t + dt$ is. We denote such probability by $P(y, t + dt)$. Since the time for a transition is dt , the balance of probability looks like

$$P(y, t + dt) = a dt P(y + \Delta y, t) + a dt P(y - \Delta y, t) + (1 - 2a dt)P(y, t) \quad (1)$$

The first two terms on the right hand side of equation (1) come from the respective forward and backward transitions from sites $y - \Delta y$ and $y + \Delta y$. The last term on the right is the probability for the particle of staying on site y . In other words, it is a conservation equation.

Now we go to the limit at which the number of sites of the discrete lattice, N , increases to infinity. Consequently, the space between site s , Δy , decreases to zero and the transition rates, a , increase to infinity.

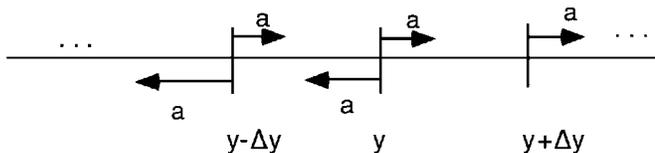


Figure 2. Any three adjacent sites of the lattice. The a 's represent transition rates.

The Limit

Since $a \rightarrow \infty$ and $\Delta y \rightarrow 0$ it is reasonable to expect that their product remains constant, in the limit. Let us denote the limit of $a (\Delta y)^2$ by D . So arranging equation (1) one gets

$$\lim_{N, a, v \rightarrow \infty; \Delta y, dt \rightarrow 0} \frac{P(y, t + dt) - P(y, t)}{dt} = \lim_{N, a, v \rightarrow \infty; \Delta y, dt \rightarrow 0} \frac{a (\Delta y)^2 [P(y + \Delta y, t) + P(y - \Delta y, t) - 2P(y, t)]}{(\Delta y)^2} \quad (2)$$

This is an equation in finite differences. One should remember that, in the limit of infinitesimally small differences, first differences become first derivatives, second order differences become second derivatives, and so on. Therefore, the final limiting equation is

$$\frac{\partial P(y, t)}{\partial t} = D \frac{\partial^2 P(y, t)}{\partial y^2} \quad (3)$$

Equation (3) is Fick's second law of diffusion (Noggle, 1989), a partial differential equation. Solving (3) is out of the scope of this paper; it can be found to be

$$P(y, t) = \frac{1}{\sqrt{4\pi Dt}} \exp\left(\frac{-y^2}{4Dt}\right) \quad (4)$$

by using Fourier transform techniques (McQuarrie, 1976).

Instead of learning how to solve (3), and similar equations, we use an alternative method which still allow to grab good physical chemical insight, the method of moments (Aris, 1956).

Temporal variation of the Moments.

The Physical Connection

It is shown that the link between the equations above with the physical world is given by the moments of the function $P(y, t)$

$$\langle y^n \rangle \equiv \int_{-\infty}^{\infty} y^n P(y, t) dy \quad (5)$$

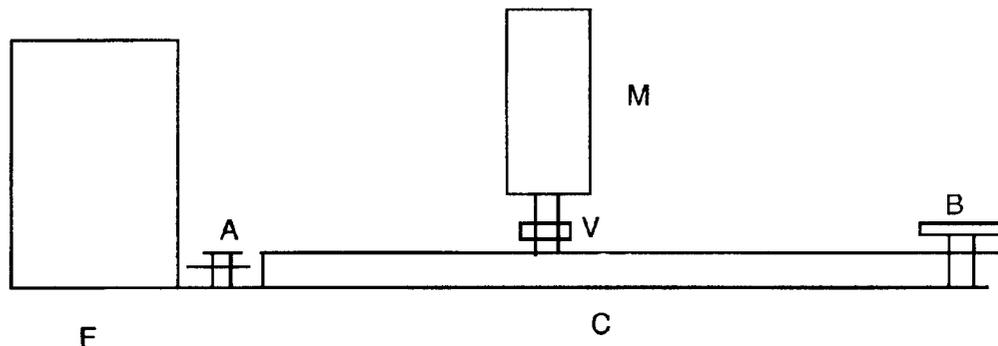
The function $P(y, t)$ in Eq. (5) is what statisticians call a density function of probability (Spiegel, 1975). It is a function normalized by the condition

$$\int_{-\infty}^{\infty} P(y, t) dy = 1 \quad (6)$$

which is nothing but a conservation condition. Physically, Eq. (6) implies that, at any time, the sum of all the contributions to the probability of finding particles is equal to the total normalized probability.

Let us visualize experimentally all what has been said

Figure 3. Experimental apparatus. M contain emulsion, F and C contains pure water.



above with equations. Think of a long column with a negligible cross section compared to its length, Figure 3. Therefore diffusion of particles along the radial direction can be neglected as a good approximation. Flask M contains a globular microemulsion.⁵ If one opens simultaneously B and V, for a very short period, then a “plug” of oil droplets enters the capillary C. These condition can be taken as the initial condition of the experiment. Observing the oil droplets diffuse longitudinally along the capillary C one could observe the random motion of these particles, product of the collisions with the molecules of the bulk phase (water). If we could measure experimentally⁶ the number density of the droplets, as a function of time, the time evolution of the system would be completely described. In principle classical mechanics allows to find such evolution; however, in practice it is impossible to keep track of the dynamic behavior of so many particles. So we need an alternative approach.

Since the particles go to the left and right with equal likelihood, the average $\langle y \rangle$ is zero. The important quantity in this case $\langle y^2 \rangle^{1/2}$, which we relate latter to some measurable quantities.

In order to compute the second moment, $\langle y^2 \rangle$, we use a technique called the method of moments (Aris, 1956). So multiplying Eq. (3) by y^n , and integrating over the whole range of y one finds

$$\int_{-\infty}^{\infty} y^n \frac{\partial P(y,t)}{\partial t} dy = D \int_{-\infty}^{\infty} y^n \frac{\partial^2 P(y,t)}{\partial y^2} dy$$

using the definition for moments, Eq. (5), and integrating by parts one gets

⁵ A microemulsion is a stable ternary system of one phase (oil or water) dispersed on a bulk phase (water or oil). The interface between the two faces is a third component (surfactant) residing at the boundary between the oil and water, whose function is to reduce the surface tension between phases and therefore stabilize the system.

⁶ By experiments of refractometry, for example.

$$\frac{d \langle y^n \rangle}{dt} = n(n-1)D \langle y^{n-2} \rangle \quad (7)$$

The temporal variation of the second moment is obtained by integrating Eq. (7), with respect to time when $n = 2$, i.e.

$$\langle y^2 \rangle = 2 Dt \quad (8)$$

Equation (8) is the key relation of all this section. Notice that the advantage of using the method of moments is that one does not need the actual functional form of $P(y, t)$ to find $\langle y^n \rangle$.

To finish this section, we point out two important relations. They allow one to do calculations of Avogadro's constant. The first quantity is the square root of the second moment

$$\lambda_y = (\langle y^2 \rangle)^{1/2} = (2 Dt)^{1/2} \quad (9)$$

The constant D can be identified with a diffusion coefficient, by either experiments measuring the root mean square of the displacement versus time. Or by straightforward, empirical dimensional analysis. At any rate, one needs an expression for D . In order to attain this task, we need to combine Stokes hydrodynamic theories (Noggle 1989) with Einstein theory of brownian motion. On Figure 4 we depict two adjacent layers y and $y + \Delta y$. The osmotic force between the two layers, as a function of the coordinate y , is equal to

$$F_{osm} = \frac{\Delta P_{osm}}{\Delta y}$$

where P_{osm} is the osmotic pressure. We use now Vant' Hoff's formula for the osmotic pressure (Noggle, 1989)

$$P_{osm} = RTM$$

T being the absolute temperature and M the number of moles of droplets per unit volume at a height y . Then F_{osm} becomes

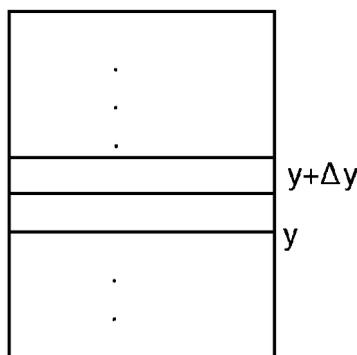


Figure 4. Perrin's vertical column.

$$F_{osm} = -R T \frac{dM}{dx}$$

From Stoke's law (Noggle, 1989), the force of friction exerted on a particle to displace it from layer y to layer $y + \Delta y$ (or viceversa) is

$$F_{fric} = -fv$$

where f stands for the friction coefficients, estimated by Stokes to be $f = 6\pi \eta r$, for spherical particles; η is the viscosity of the fluid (water in our case). Moreover, v is the constant velocity attained by the particle in its migration.

One can write

$$v = - \frac{F_{fric}}{f}$$

In order to identify F_{fric} with the osmotic force F_{osm} , one needs to consider that the force F_{osm} is actually divided between $M N_0$ molecules.⁷ So one effectively has the velocity modified by a factor $M N_0$, i.e.

$$v = - \frac{F_{osm}}{M N_0 f}$$

or

$$Mv = - \frac{F_{osm}}{N_0 f} = R \frac{T}{N_0 f} \frac{dM}{dx}$$

The units of the quantity on the left hand side correspond to a flux. Additionally, the right hand side is a constant times a first derivative of concentration with respect to position. So

one can identify this expression with Fick's first law of diffusion, and therefore conclude

$$D = \frac{R T}{N_0 f}$$

Substituting f in the denominator, and using Eq. (9) we finally obtain

$$N_0 = \frac{t}{\lambda_y^2} \cdot \frac{R T}{3 \pi \eta r} \tag{10}$$

t is the time interval for which we make the observation, r is the radius of the suspended oil droplets, η is the coefficient of viscosity of the liquid, in our case water. R is the universal gas constant, and T is the absolute temperature at which the experiment is performed.

We have developed all the theoretical background necessary for our purposes. Now we move to the practical world of experiments. There are complicated experimental details that our discussion so far has not considered, i.e. how to make oil droplets with the same radius, and how to determine that radius. The next section deals with these issues.

The Experiments of Jean Perrin

Jean Perrin is the outstanding experimentalist in the history of Brownian Motion. His contribution to science is fundamental since his experiments proved the existence of atoms.

The experiments

The experimental setup of Perrin's experiments is schematized in Figures 4 and 5. One starts with an emulsion resin/water. Because of the gravitational field, the number of droplets per unit volume (number density), n , varies as a function of height. This is schematized in Figure 4 by two adjacent "layers" y and $y + \Delta y$. One can notice that the higher the distance the smaller the number density.

Since the two layers y and $y + \Delta y$, in Figure 4, have different number densities, there must be an osmotic pressure from the most concentrated to the least concentrated. From the kinetic theory of gases (Noggle, 1989) the osmotic pressure is equal to $2/3 nW$; where n is the number density and W is the mean kinetic energy. The difference in osmotic pressure between the two layers y and $y + \Delta y$ then is

$$P_{osm} = \frac{2}{3} W \Delta n,$$

where Δn is equal to the difference in number density between the layers. Therefore the osmotic force is equal to the product of the area of the cross section, s , of the column in Figure 4 times P_{osm} . That is

⁷ Remember that M is the molarity, i.e. the number of moles of droplets per unit volume. So the total number of droplets is M times Avogadro's number, N_0 .

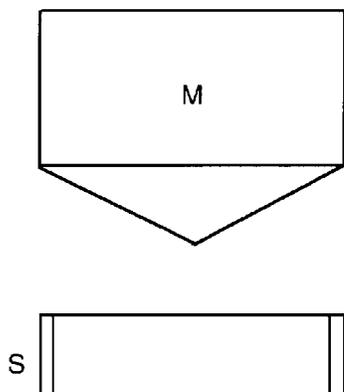


Figure 5. Diagram representing Perrin's experimental setting. M is a microscope and s is a sample of emulsion.

$$F_{osm} = \frac{2s}{3} W \Delta n$$

On the other hand, the weight of the droplets need to be corrected for the “push” that buoyancy exerts on them. Calling ρ_{drop} and ρ_{water} the densities of the droplets and the solvent, and using formulas from elementary physics, we find the correct gravitational force to be

$$F_{grav} = ns \Delta h v_{drop} (\rho_{drop} - \rho_{water}) g$$

where v_{drop} is the volume of the droplet and g is the constant gravitational acceleration.

At equilibrium

$$F_{osm} = F_{grav}$$

so one gets

$$\frac{2}{3} W \frac{\Delta n}{n} = \Delta h \frac{4}{3} \pi r^3 (\rho_{drop} - \rho_{water}) g$$

integrating last equation from (h_0, n_0) to (h, n) one finds

$$2.303 W \log \frac{n_0}{n} = 2 \pi r^3 h (\rho_{drop} - \rho_{water}) g \quad (11)$$

for spherical droplets of radius r .

When one substitutes in Eq. (11) the kinetic energy of a monoatomic gas, $\frac{2}{3} \frac{RT}{N_0}$, a calculation of Avogadro's constant N_0 is possible. Notice that the experimentally difficult quantities to determine in Eq. (11) are the number densities n_0 and n .

What Perrin did to determine number densities

Perrin (1908, 1914) and his students measured the density using a procedure that we summarize as follows

a) Form a uniform emulsion using the method of fractional centrifugation.

b) Determine the radius of the particles with a microscope.

c) Use a very small sample of emulsion, and analyze it in a microscope, Figure 5. Varying the distance of the objective lens one can count (by taking instantaneous pictures) the number density as a function of height by just considering particles in focus. In other words, neglect the particle out of focus.

The best value that Perrin (1908) obtained for Avogadro's number was:

$$N_0 = (6.5 \pm 0.6) \times 10^{23}$$

Conclusions

We have analyzed a phenomenon which has a fundamental connection with the microscopic world of atoms and molecules.

The key point of the paper comes in our discussion about the determination of Avogadro's number by Perrin. Something really relevant to notice is the almost “symbiotic” relation that theoretical thinking has with the experimental world. For example, Perrin used the kinetic theory of heat to measure N_0 .

We end up this section making a calculation of N_0 using constants from three different sources. We evaluate

$$N_0 = \frac{t}{\lambda_y^2} \cdot \frac{RT}{3\pi\eta r} \quad (12)$$

for the diffusion of atoms of Argon in water when t is equal to one second. The diffusion coefficient at 298 K is (Lide, 1991)

$$D = 2.00 \times 10^{-5} \frac{\text{cm}^2}{\text{s}}$$

The viscosity of water at 298 K is (Noggle, 1989)

$$\eta_{water} = 8.937 \text{ mp}$$

We take the atomic radius of Ar from Oxtoby's book (Oxtoby *et al.*, 1990)

$$r = 0.97 \text{ \AA}$$

For an interval of one second, we get using Eq. (9)

$$\lambda_y = 4.472 \times 10^{-3} \text{ cm}$$

and

$$N_0 = 15 \times 10^{23}$$

We obtain the correct order of magnitude for Avogadro's number, but a really bad precision. That is not so tragic

considering that we used data from several sources; also the atomic radius of Ar was taken from X-ray experiments, which analyze the solid structure of Ar and neglect solvation effects in water. Furthermore, Eqs. (9) and (10) might not hold for something as light and small as Ar.

We believe the methodology and concepts introduced in this paper could be well used by some instructors in their lectures.

Literature cited

Aris, R., *Proc. R. Soc. London Ser. A* **235**, 67-77, 1956.
 Berry, R.S., Rice, S.A., Ross, J., *Physical Chemistry*, John Wiley, New York, 1980, part two, Chapter 20.
 Brown, R., *Phil. Mag.*, **4**, 161-173, 1828.
 Einstein, A., *Investigations on the Theory of Brownian Movement*,

Dover: New York, 1956.
 Lide, D.R., Ed., *Handbook of Chemistry and Physics*, CRC: Boston, 1991.
 McQuarrie, D.A., *Statistical Mechanics*, Harper and Row, New York, 1976.
 Noggle, J.H., *Physical Chemistry*, Scott, Foresman and Co., Boston, 1989, Chapter 9.
 Oxtoby, D.W., Nachtrieb, N.H., Freeman, W.A., *Chemistry: Science of Change*, Saunders College Publishing, Orlando, FA, 1990, Chapter 18.
 Perrin, J., *Ann. de Chim. et de Phys.*, 1-114, 1908.
 Perrin, J., *Comptes Rendus*, **158**, 1168-1171, 1914.
 Spiegel, M.R., *Probability and Statistics*, Schaum's Outline Series, McGraw-Hill, New York, 1975, Chapter 3, p. 79.
 Smolochowski, M.V., *Ann. d. Phys.* **25**, 205, 1908.

III Jornadas de la Enseñanza Universitaria de la Química

10 al 12 de noviembre de 1997
 Complejo Vaquerías-Huerta Grande-Córdoba, Argentina

Organiza: AQA- Asociación Química Argentina - Grupo de Especialistas Universitarios en la Enseñanza de la Química
 UNC - Universidad Nacional de Córdoba - Fac. de Ciencias Agropecuarias - Fac. de Ciencias Exactas, Físicas y Naturales
 UTN - Universidad Tecnológica Nacional - Facultad Regional Córdoba

Contenido: ■ Conferencias plenarias ■ Mesas redondas
 ■ Comunicaciones libres ■ Talleres de trabajo

Costos:	<i>Fecha</i>	<i>Inscripción</i>	<i>Alojamiento 3 días pensión completa en Vaquerías</i>
	hasta el 30/4/1997	\$ 30	\$ 120
	hasta el 30/6/1997	\$ 50	\$ 150
	desde el 1/7/1997	\$ 70	\$ 180

Presentación de resúmenes: fecha límite 30/6/1997

Informes: Ing. Beatriz Maroto, UNC - Fac. de Cs. Agropecuarias
 CC. 509 (5000) Córdoba - Argentina, Fax: +54 - 51 - 334118
 E-mail: bmaroto@agro.uncor.edu
 hector@sa.frc.utn.edu.ar
 hector@utnfrc.edu.ar