

Avogadro number hystorical review

- 1805 Atomic hypothesis by Dalton
- 1811 Avogadro law
- 1814 Ampère proposes de same law
- 1820-1830 The measure of the gaz density gives the atomic weights larger then those proposed by Dalton. Avogadro is forced to introduce a new hypothesis: existence of integrand molecules and elementary molecules.
- 1836 J.B. Dumas in his lessons at “Collège de France” condemns the Avogadro Law as “ trop obscure et coûteuse en hypothèses”
- 1853 Gerhardt renews the Avogadro law using for the first time the words atomes and molecules.
- 1856 Mendeleiev periodic table of elements.

Perrin works

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MOUVEMENT BROWNIEN ET RÉALITÉ MOLÉCULAIRE.

(*Ann. Chimie et Physique*, 8^e série, 18, 1909, p. 1-114.)

The question for Perrin is to prove experimentally that the Brownian motion is produced by the molecular collisions on the particles

For this he needs to know the value of the Avogadro number

Avogadro number first determination

Perrin's works

- Discussion on how the order of magnitude of the Avogadro number can be estimated.
 - a) viscosity, mean free path and the density difference between gas and liquid
 - b) from the coefficient of Van der Waals equation
- Experiments on segregation of very small grains ($1\mu\text{m}$) in water
Weight compared to osmotic pressure
 - a) measure of the grain mass
 - c) measure of the grain radius
(Stokes law, direct counting)
 - d) Direct counting of grains as function of the height.
- Experimental test of the Einstein's law on Brownian motion.

Estimate the order of magnitude of N_A

$$L = \text{mean free path} = (\sqrt{2}\pi D^2 n)^{-1}$$

$$n = \text{molecule density} = N_A/V_M$$

$$D = \text{molecule diameter}$$

$$\eta = \text{dynamic viscosity} = \frac{\rho_g \bar{v} L}{3}, \quad \Rightarrow \quad L = \frac{3 \eta}{\rho_g \bar{v}}$$

$$\text{where} \quad \bar{v} = \sqrt{\frac{8K_B T}{\pi m}} = \sqrt{\frac{8RT}{\pi M}}$$

From the measure of the gas viscosity one can determine L

Method to estimate the minimum possible value of N_A

$$D = \left(\sqrt{2} L \pi \frac{N_A}{V_M} \right)^{-1/2}$$

D is a function of N_A and another equation is needed

The maximum volume occupied by N molecules is 73% of the totally available volume.

If V_L is the volume of the gas in the liquid phase then:

$$\frac{\pi}{6} N D^3 < 0.73 V_L \quad \Rightarrow \quad \frac{\pi}{6} \frac{N_A D^3}{V_M} < 0.73 \frac{V_L}{V_M}$$

$$N_A > \frac{V_M}{170.5 \varphi^2 L^3} \quad \text{with} \quad \varphi = \frac{V_L}{V_M} = \frac{\rho_g}{\rho_L}$$

with $L = \frac{3\eta}{\rho_g} \sqrt{\frac{\pi M}{8RT}}$

Difficult to have a precise measurement of η

Gas viscosimeter

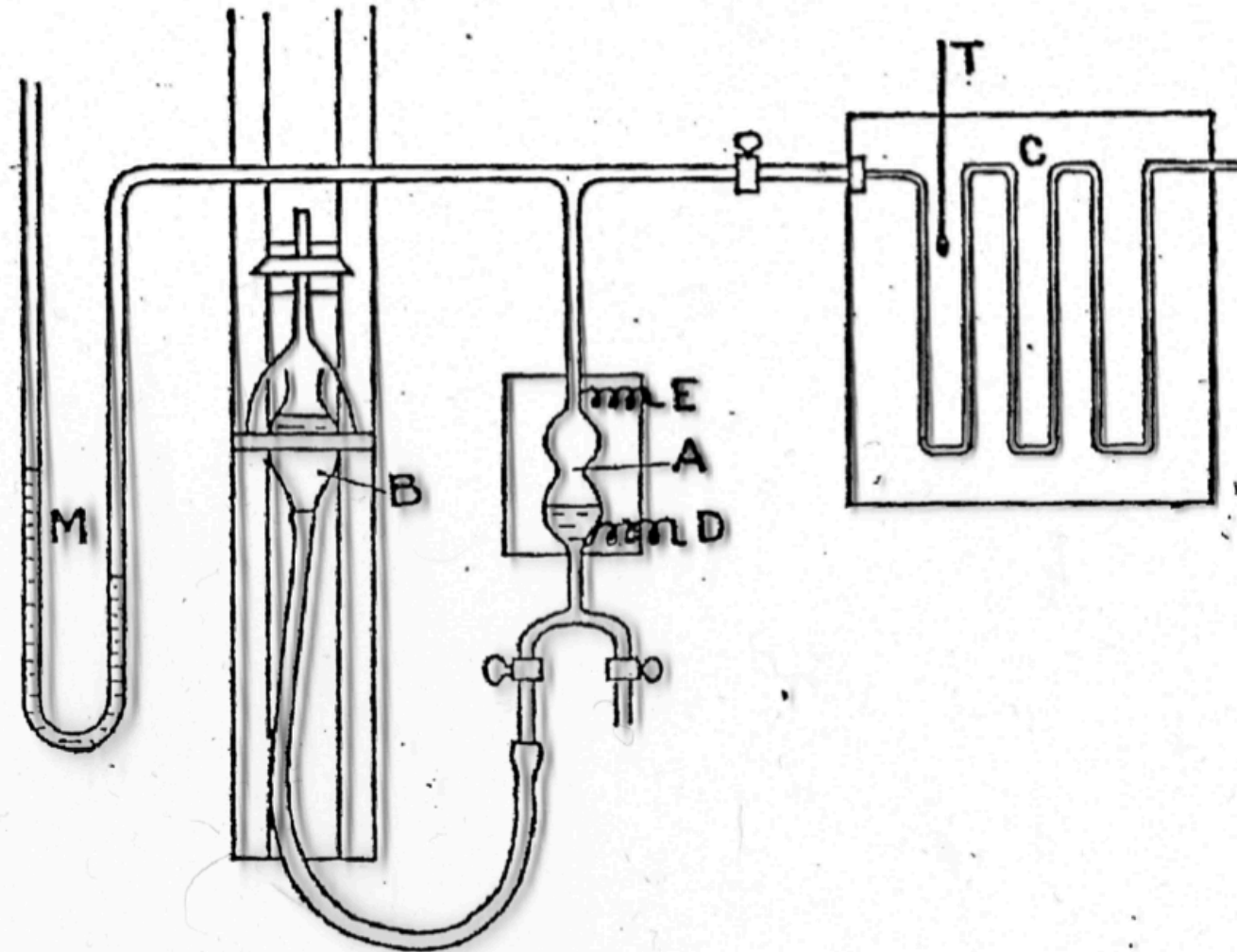


FIG. 1.9 a.

Computed values of N_A

Gaz	b ($10^{-5}m^3$)	φ (10^{-4})	η ($\mu Pa s$)	L (nm)	M (Kg)	D ($10^{-10} m$)	I st method N_A 10^{23}
H_g	5.5	7	44	110	0.2	2.6	3
N_2	3.8	13	18	88	0.028	2.9	1
O_2	3.2	10	21	95	0.032	2.7	1.5
Ar	3.22	11	23	94	0.04	2.7	1.30
CO_2	4.29	16	20	77	0.044	3.0	1.1

IInd method to estimate the value of N_A

$$\left(p + \frac{a}{V_M^2}\right)(V_M - b) = RT \quad \text{Van de Waals equation}$$

with $a = 3P_c V_c^2$ and

$b = 4V_m N_A$ where $V_m = \pi D^3/6$ is the volume of a molecule.

As a consequence : $b = \frac{2\pi}{3} D^3 N_A$

Using: $D = \left(\sqrt{2} L \pi \frac{N_A}{V_M}\right)^{-1/2}$

we get $N_A = \frac{\sqrt{2} V_M^3}{9\pi b^2 L^3}$ where L is determined from viscosity measurements

Measure of gas equation of state

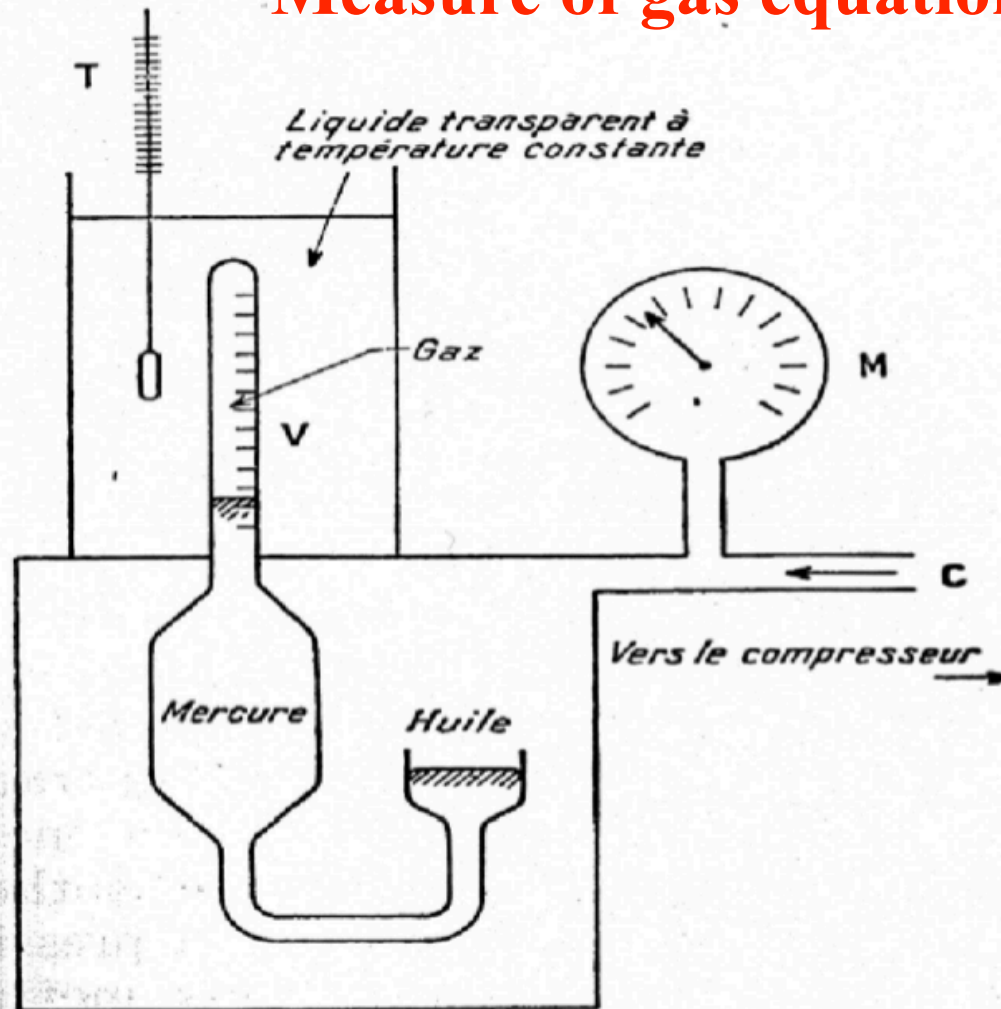


FIG. 58. — Représentation schématique de l'appareil de Cailletet : I, thermomètre ; M, manomètre ; V, tube gradué pour la lecture du volume.

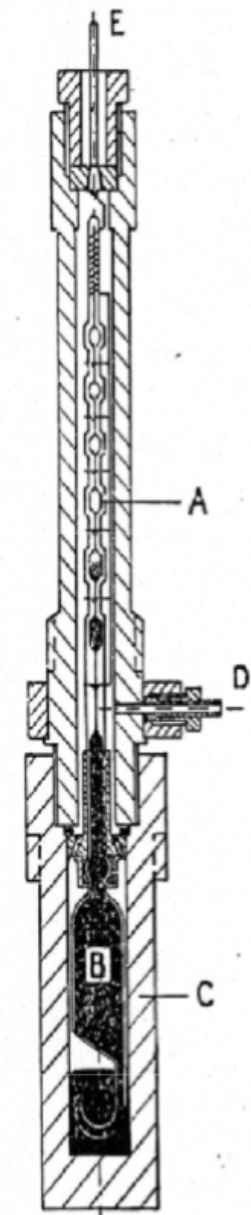


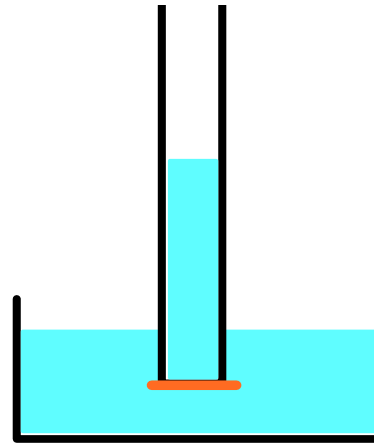
FIG. 59.

Computed values of N_A

Gaz	b ($10^{-5}m^3$)	φ (10^{-4})	η ($\mu Pa s$)	L (nm)	M (Kg)	D ($10^{-10} m$)	I st method	II nd method
							N_A 10^{23}	N_A 10^{23}
H_g	5.5	7	44	110	0.2	2.6	3	4.5
N_2	3.8	13	18	88	0.028	2.9	1	5.21
O_2	3.2	10	21	95	0.032	2.7	1.5	6.2
Ar	3.22	11	23	94	0.04	2.7	1.30	6.2
CO_2	4.29	16	20	77	0.044	3.0	1.1	6.4

Direct determination I

Osmotic pressure



Osmotic pressure of a colloidal solution of identical grains

- Hp: 1) Because of the shocks with the other grains each layer is submitted to an osmotic pressure
- 2) This pressure can be computed as in a gas

$$P = \frac{2}{3}nW$$

W = kinetic energy of the grains

n = density of grains

Direct determination II

$$\frac{2}{3}W \log\left(\frac{n_0}{n}\right) = \varphi_g(\rho_g - \rho_w)gh$$

ρ_g = grain density, ρ_w = water density

φ_g = volume of a grain = $\frac{4\pi a^3}{3}$

Three problems:

- how to produce an emulsion of identical grains
- how to determine the mass of the grains
- how to determine the radius of the grains

Preparation of the emulsions

- Choice of the material. (natural resins such as latex, rubber glue)
- Grain production.
 - a) Dissolution of the resin in methyl alcohol
 - b) Dissolution with waterresult: white emulsion with almost spherical grains of very different sizes
- Size selection obtained by a centrifugal process and a dilution in water applied several times
- Measure of the grain density obtained by weight.
 - a) Volume V of the test tube.
 - b) measure of the solution mass m'
 - c) drying of the water
 - d) measure of the total grain mass μ

$$V - \frac{m' - \mu}{\rho_w} = V_g = \text{total grain volume} \quad \Rightarrow \quad \rho_g = \mu / V_g$$

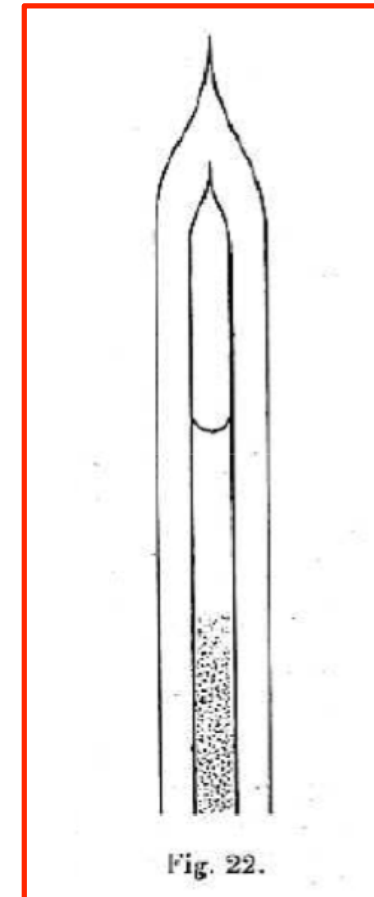
Measure of the grain radius (I)

Two methods are used.

I) Stokes law :
$$6\pi\eta av = \frac{4}{3}\pi a^3(\rho_g - \rho_w)g$$

- Measure of the falling speed in a capillary tube to avoid convective motions
- The measurement is done looking at the transparency of an emulsion day after day

Problem: Perrin did not know whether the Stokes law can be applied at very small particle ($\sim 1\mu\text{m}$)



Measure of the grain radius (II)

II) Direct counting

- Use a water-grain solution with a known mass of grain
- Add acid to the solution (0.01 mole/litre)
- Depose a drop of this solution on a microscope test glass
- Wait for the grain sticking on the glass surface
- Wait for the total evaporation of the water
- Direct count of the grain (11000 grains counted)

$$\frac{\text{Total mass of grains}}{\text{Counted number of grains}} = \frac{4}{3} \pi a^3 \rho_g$$

The agreement of the results of the two methods was the first experimental proof that the Stokes law can be used at small scales

Perrin in his article comments that it will be interesting to know the limiting scale of this law.

Measure of the density as function of the height

$$\frac{2}{3}W \log\left(\frac{n_0}{n}\right) = \frac{4\pi a^3}{3}(\rho_g - \rho_w)gh$$

Perrin's experimental set-up

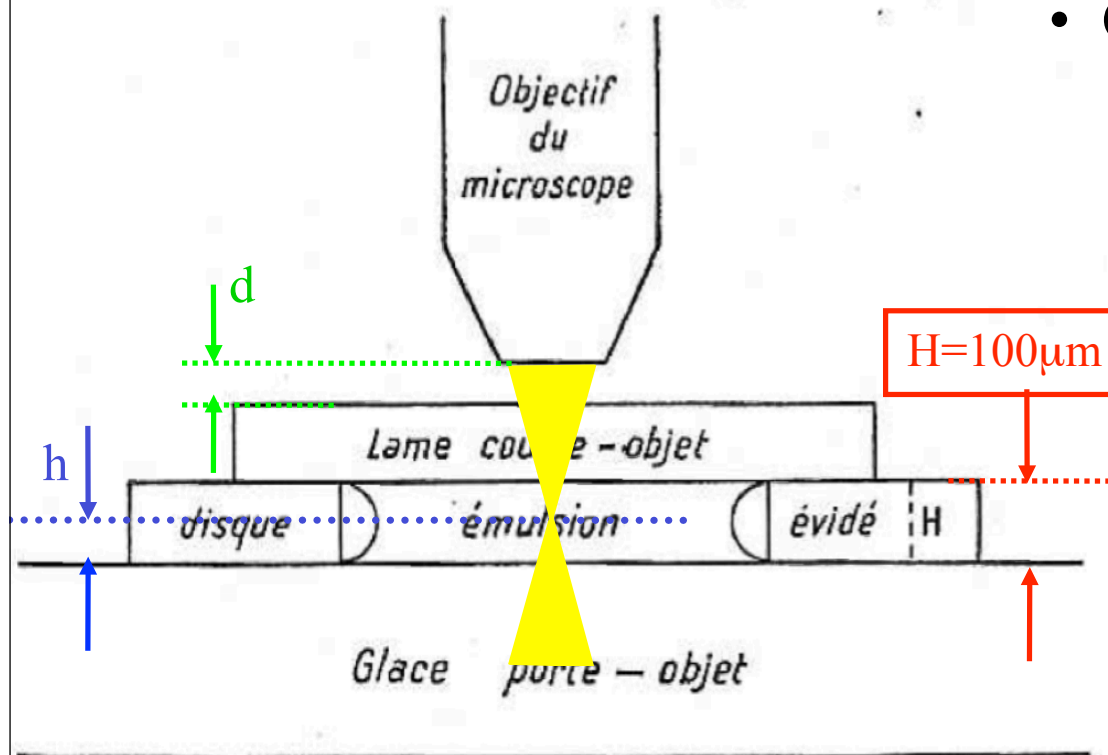


Fig. 21.

- Count of the grains number as a function of h

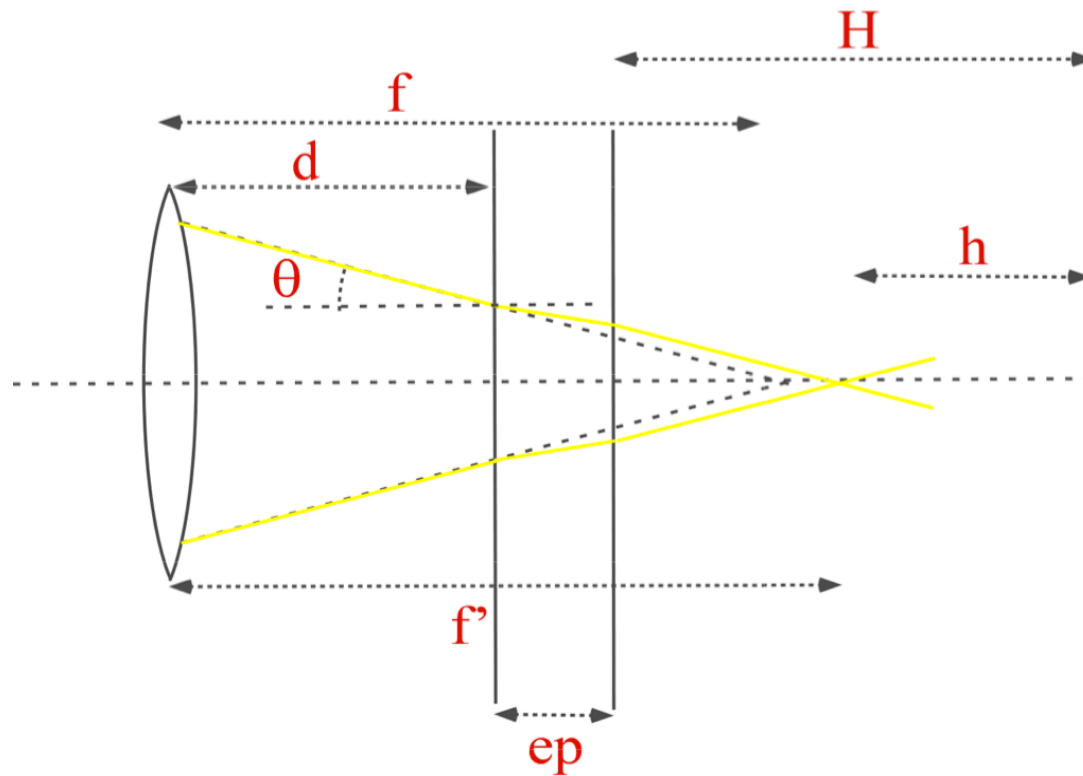
Microscope features

- very low field depth
- good horizontal and vertical resolutions

Problem:
measure of h

Measure of h

Because of the thickness of the top plate $\delta h = \delta d \frac{n_2}{n_1}$



Field depth of the objective: $\delta f = \lambda \frac{f^2}{D^2}$

Image of the grains

PLANCHE I.



Two counting methods

1. Diaphragm on the ocular lens. At each value of h
 - a) image taken each 15s
 - b) count of the particle which are seen in the image.
2. Used for particles of about 2 or 3 μm .
Direct count of the particles as a function of h .

peu différents des nombres :

100, 45, 21, 9,4,

qui sont en progression géométrique.

On voit l'un au-dessus de l'autre, dans la figure 24, des dessins qui reproduisent la distribution des grains dans quatre des photographies qui ont conduit aux nombres précédents; la raréfaction progressive est évidente. Cette raré-

Measure of the density as function of the height

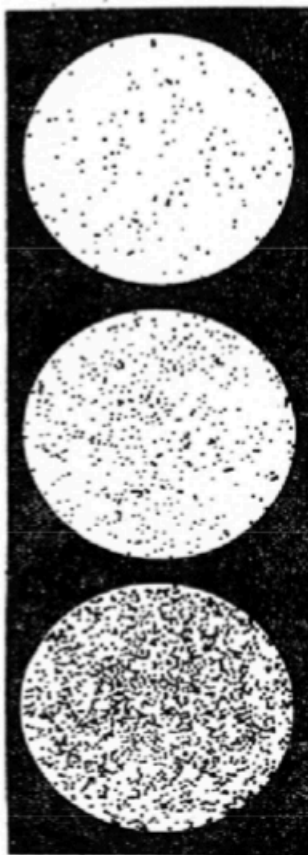
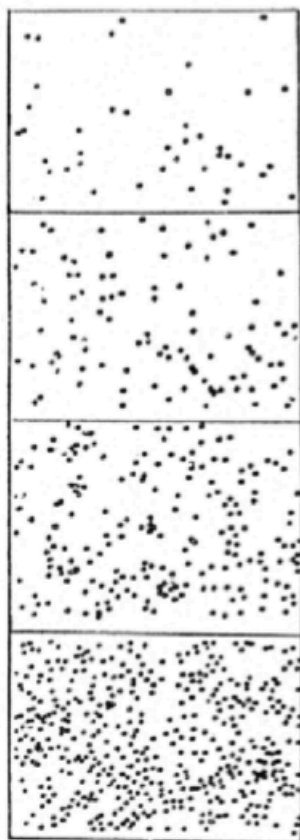
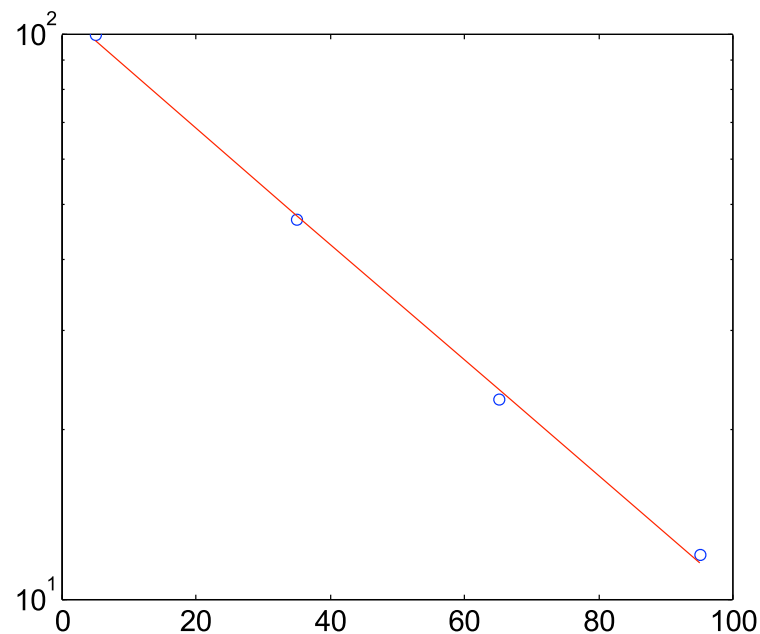


Fig. 24.

Répartition d'équilibre de grains de gomme-gutte $0,5 \mu$ de diamètre; 4 niveaux pris de 10 en 10μ .

Fig. 24 bis.

Répartition d'équilibre d'une émulsion de mastic (1μ de diamètre, 3 niveaux pris de 12 en 12μ).



faction est frappante lorsque, gardant les yeux fixés sur la préparation, on soulève rapidement le microscope en agissant sur sa vis micrométrique. On voit

Quantitative measure

$$\frac{2}{3}W \log\left(\frac{n_0}{n}\right) = \varphi_g(\rho_g - \rho_w)gh$$

ρ_g = grain density, ρ_w = water density

φ_g = volume of a grain = $\frac{4\pi a^3}{3}$

What W is ?

Perrin: “ Si notre théorie cinétique est exacte W ne dépendra pas de l’émulsion choisie et elle sera égale à l’énergie moyenne d’une molécule quelconque à la même température. “

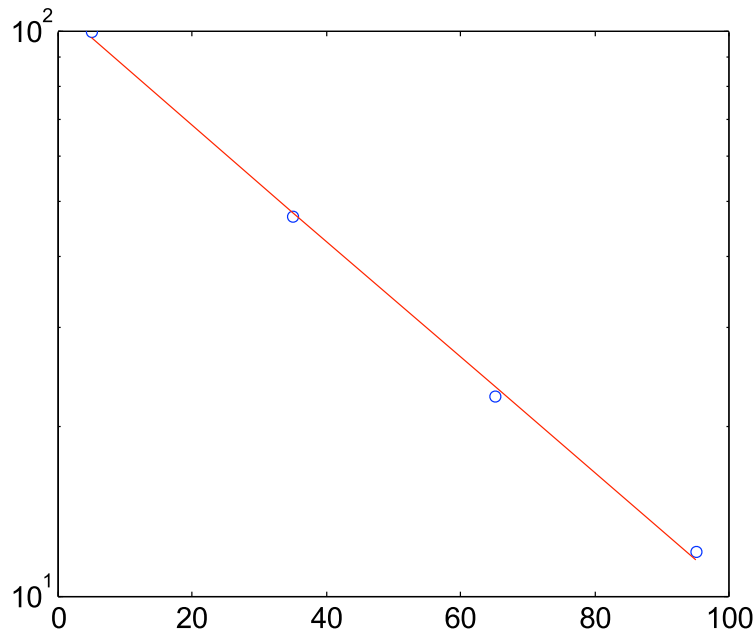
$$W = \frac{3 R T}{2N_A}$$

$$R T \log\left(\frac{n_0}{n}\right) = \varphi_g(\rho_g - \rho_w)g N_A h$$

Quantitative measure

$$\log(n) = -\frac{\varphi_g(\rho_g - \rho_u) g N_A h}{R T} + \log(n_o)$$

Two methods



I) Linear fit of the data

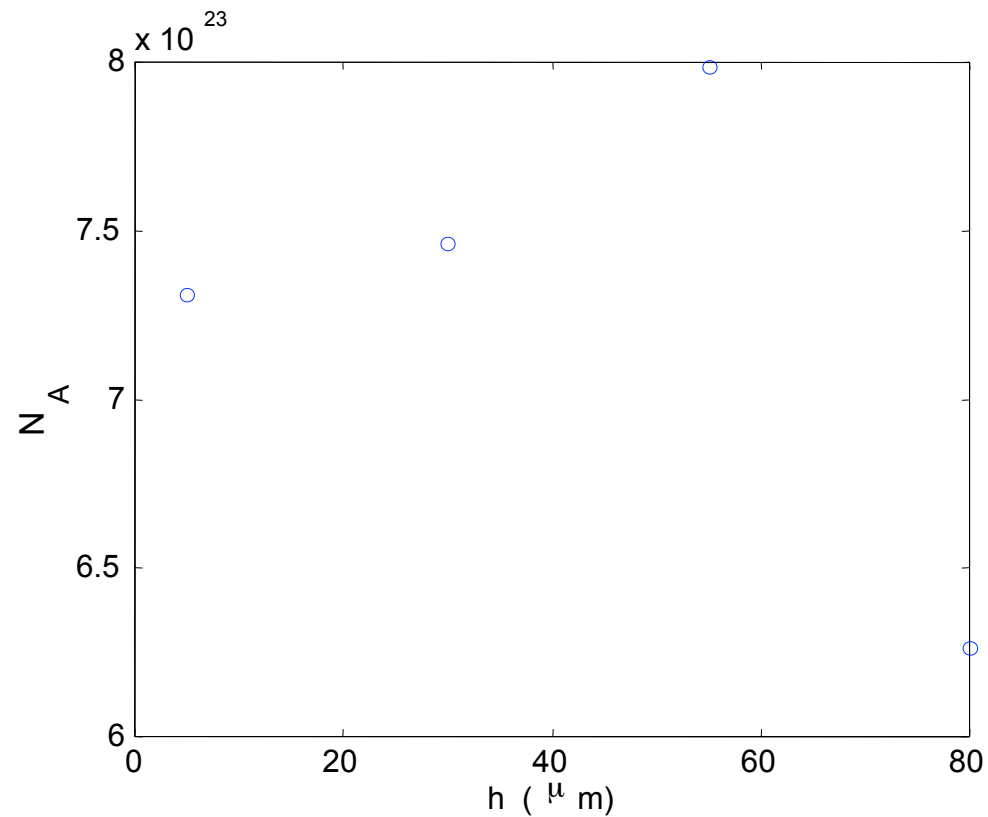
$$\log(n) = A h + B$$

$$N_A = \frac{3 R T A}{4 \pi a^3 g (\rho_w - \rho_g)}$$

II) Local calculation

$$N_A(h) = \frac{3 R T}{4 \pi a^3 g (\rho_w - \rho_g)} \frac{\log(n(h_0)/n(h))}{(h-h_0)}$$

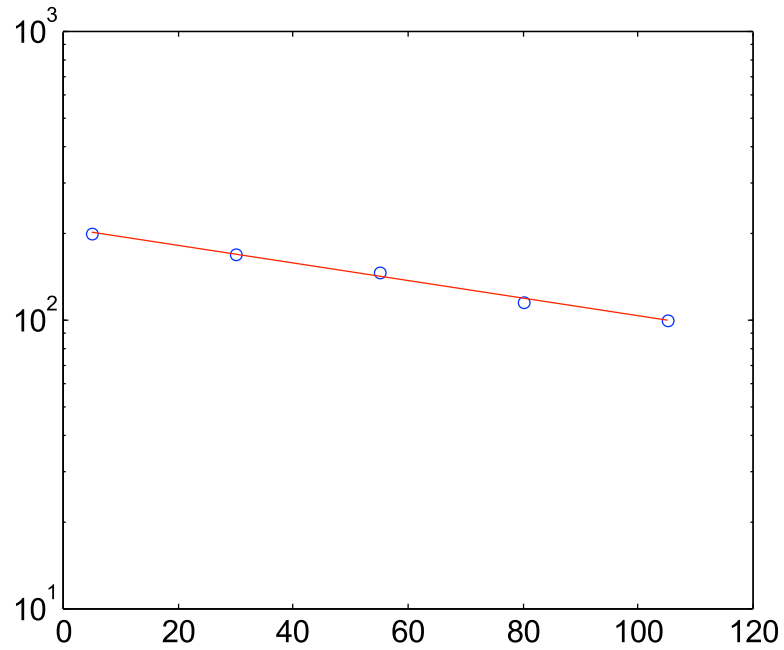
$$N_A(h) = \frac{3 R T}{4 \pi a^3 g(\rho_w - \rho_g)} \frac{\log(n(h_0)/n(h))}{(h-h_0)}$$



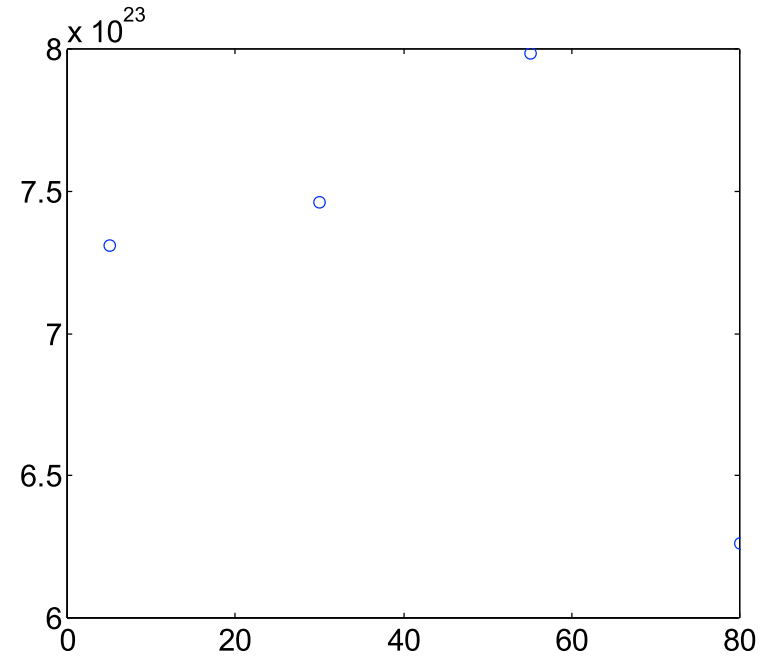
$$\tilde{N}_A = \langle N_A(h) \rangle \pm \delta N_A$$

Results

Latex, particle density = 1.205, radius in micron = 0.14

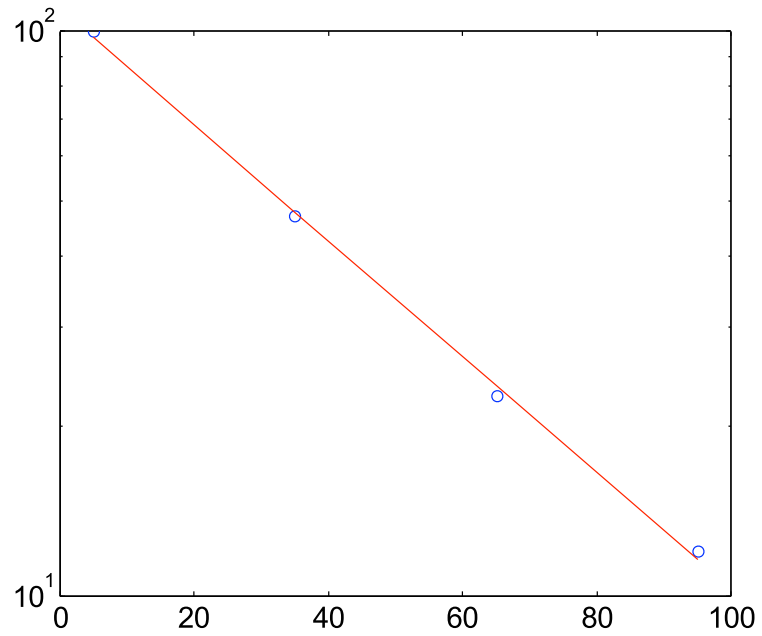


$$W^V = 1.2 \cdot 10^{23} (1 \mp 0.01)$$

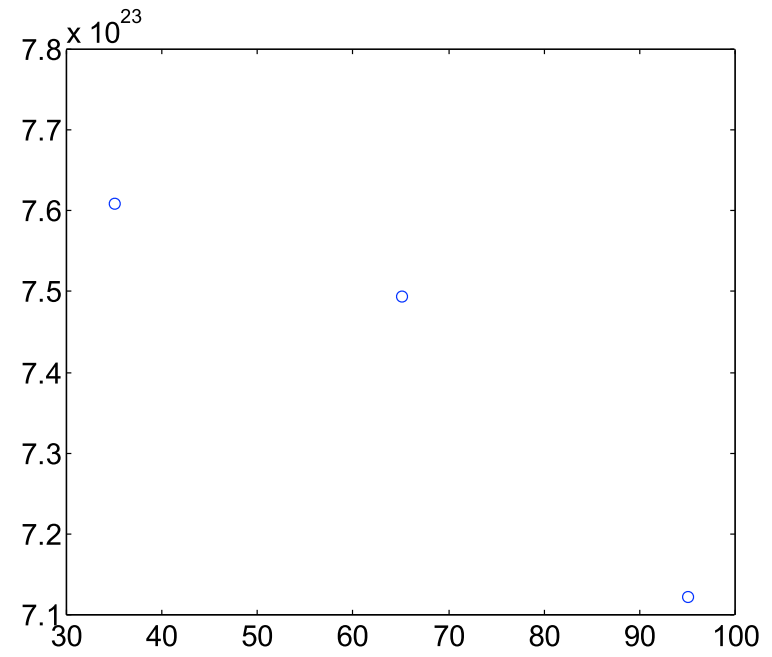


$$W^V = 1.3 \cdot 10^{23} (1 \mp 0.1)$$

Latex , particle density = 1.206, radius in micron = 0.212

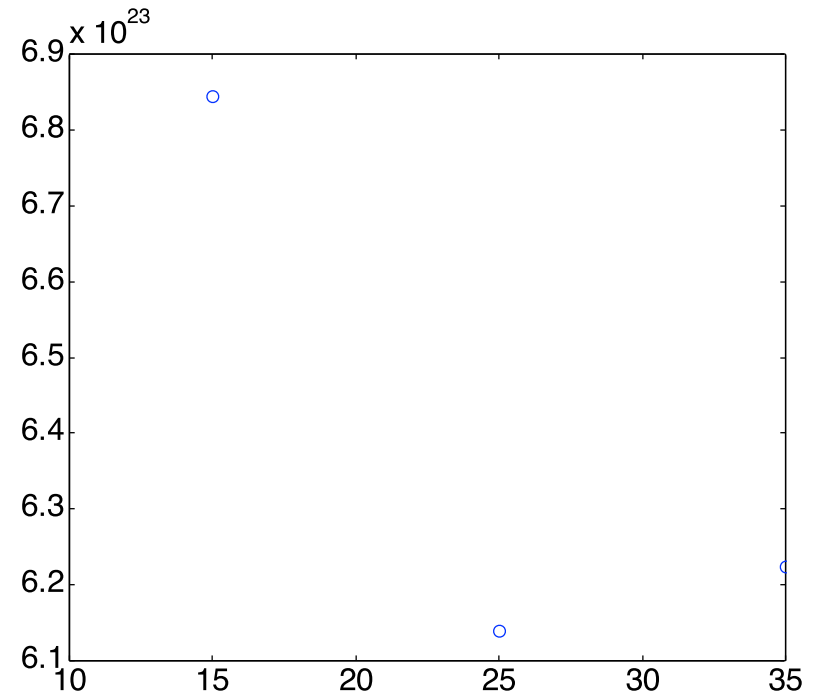
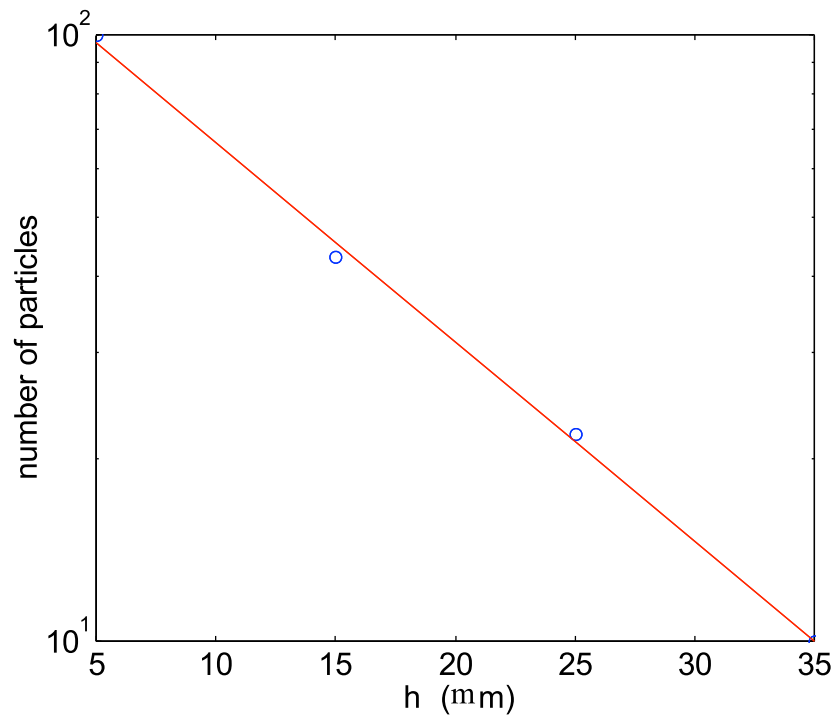


$$N_A = 7.2 \cdot 10^{23} (1 \pm 0.01)$$



$$\tilde{N}_A = 7.4 \cdot 10^{23} (1 \pm 0.03)$$

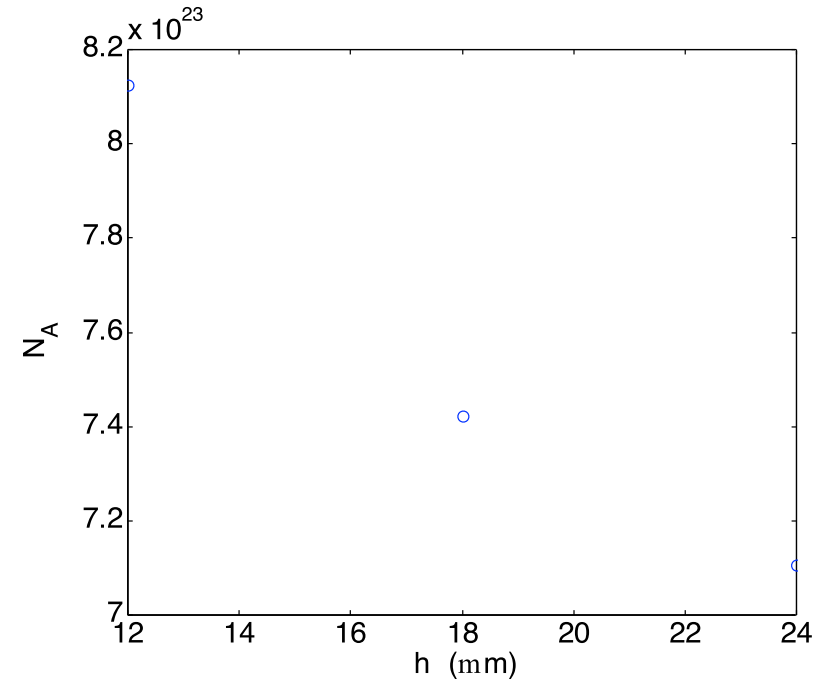
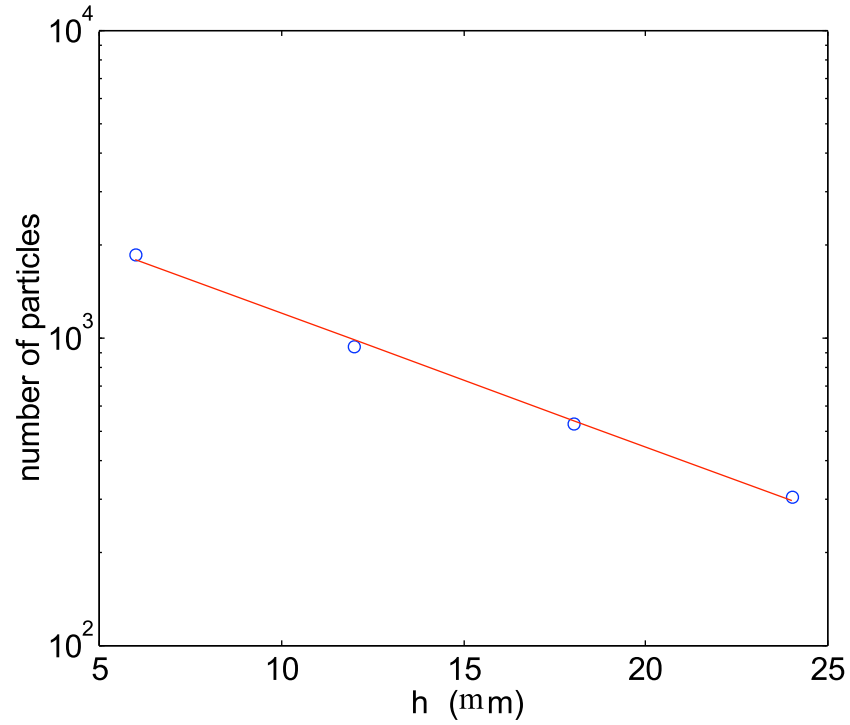
Latex, particle density = 1.3, radius in micron = 0.29



$$N_A = 6.1 \cdot 10^{23} (1 \pm 0.01)$$

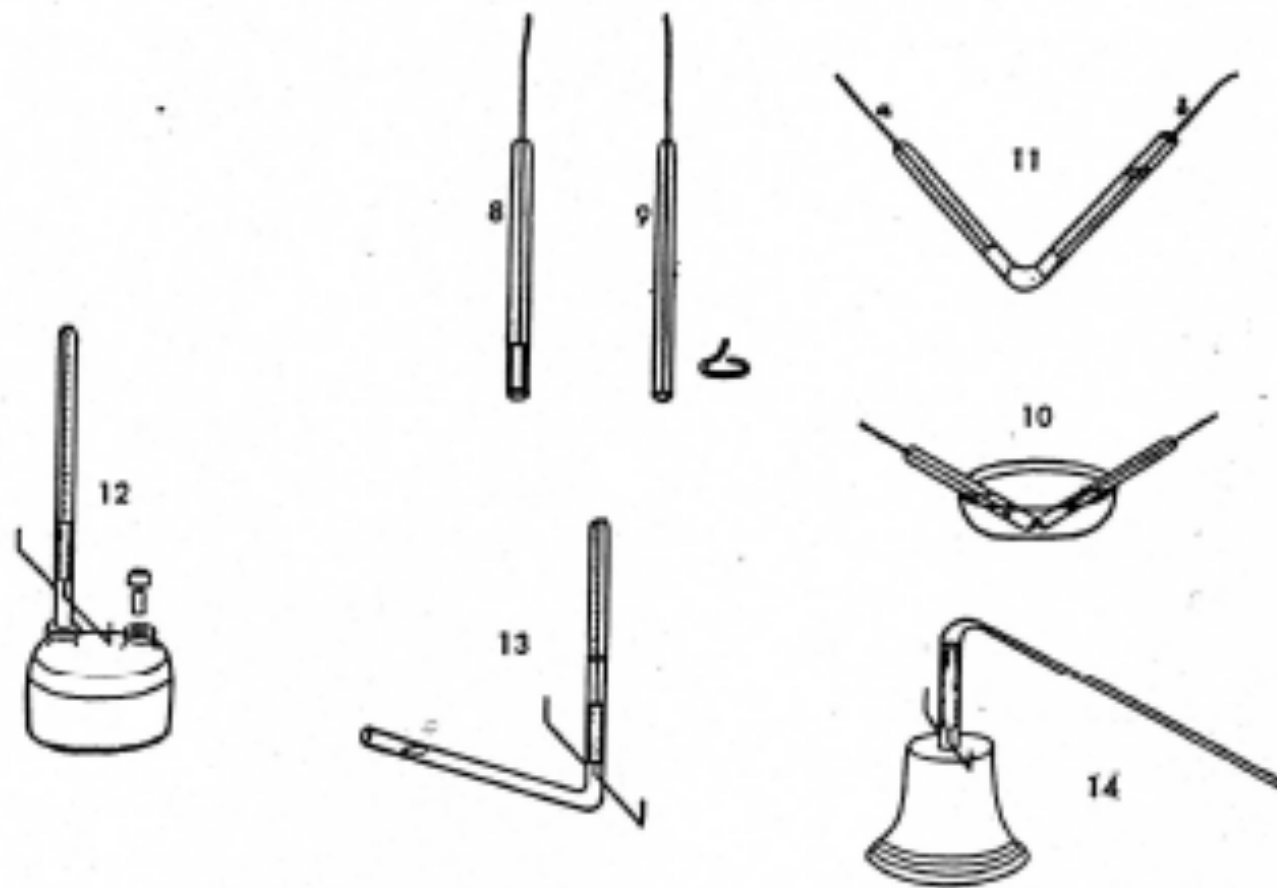
$$N_A = 6.1 \cdot 10^{23} (1 \pm 0.01)$$

Rubber glue, particle density = 1.06, radius in micron = 0.52



$$N_A = 7.0 \cdot 10^{23} (1 \pm 0.01)$$

$$\tilde{N}_A = 7.5 \cdot 10^{23} (1 \pm 0.07)$$



Figs. 8-14

with their mouths near to each other that ...

Brownian motion

Simple derivation:

The starting point is the diffusion equation

$$\frac{\partial n}{\partial t} = D \frac{\partial^2 n}{\partial x^2}$$

whose solution is $n = \frac{1}{\sqrt{4\pi Dt}} \exp\left(-\frac{(x-x_0)^2}{4Dt}\right)$

which implies: $\langle x^2 \rangle = x_0^2 + 2Dt$

(in 3 dimensions is $\langle r^2 \rangle = r_0^2 + 6Dt$)

Brownian motion

Experiments on segregation have shown that:

$$m g n(z) = -\frac{dn}{dz} \frac{RT}{N} \quad \text{with } m = (\rho_g - \rho_w) \varphi_g$$

This equation can be derived from kinematic conditions.

In presence of gravity: $6\pi\eta a \bar{v} = -mg$

The flux of falling particles is $\Phi = -\frac{m g n(z)}{6\pi a \eta}$.

This flux is balanced by diffusion $D \frac{dn}{dz}$ and $\frac{dn}{dz} = -\frac{m g n(z)}{6\pi D a \eta}$

Comparing $\frac{dn}{dz}$ obtained from the two equations then: $D = \frac{R T}{6 N_A \pi a \eta}$

Using the solution of the diffusion equation:

$$\langle x^2 \rangle = \frac{R T \tau}{3 N_A \pi a \eta}$$

independent of the particle mass

Measure

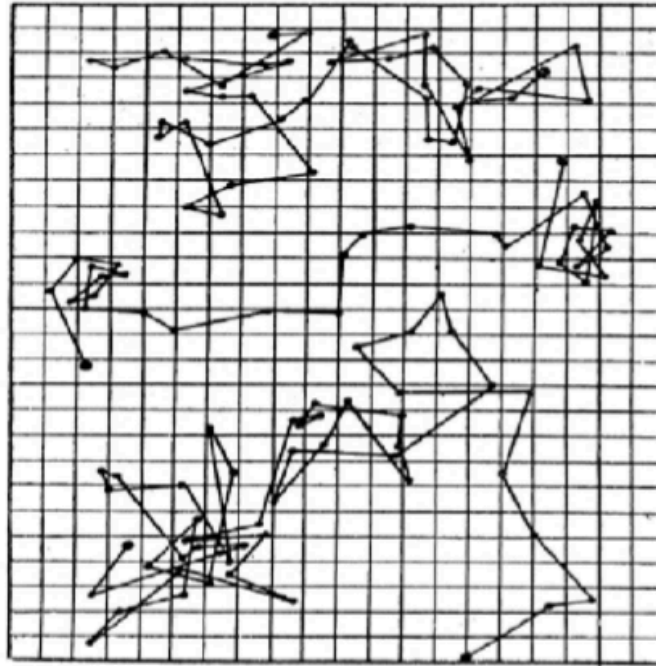


Fig. 25.

31. LA LOI DE RÉPARTITION DES DÉPLACEMENTS. — Nous avons dit (n° 27) que, dans le cas de grains ayant la densité du liquide intergranulaire, les déplacements en un temps donné doivent se répartir autour du déplacement moyen selon la loi d'irrégularité de Maxwell (n° 9). Il est utile de vérifier directement cette loi si importante. Cela peut se faire de diverses façons.

D'abord, la probabilité pour que la composante selon Ox soit comprise entre x et $x + dx$ doit être

$$\frac{1}{\xi} \frac{1}{\sqrt{2\pi}} e^{-\frac{x^2}{2\xi^2}} dx,$$

en désignant toujours par ξ^2 le carré moyen de la composante x , résultat qui restera valable pour tout axe horizontal quand les grains n'auront plus la densité du liquide intergranulaire (n° 27)

Sur \mathcal{N} observations, le nombre de celles qui donneront des composantes comprises entre x_1 et x_2 sera donc calculable par l'expression

$$\mathcal{N} \frac{1}{\xi} \frac{1}{\sqrt{2\pi}} \int_{x_1}^{x_2} e^{-\frac{x^2}{2\xi^2}} dx.$$

M. Chaudesaigues a fait ce calcul relativement à un axe horizontal arbitraire,

égale à la somme des carrés des segments, en sorte que pour avoir le carré moyen de la projection sur un axe, il suffit de mesurer un à un ces segments, de calculer leurs carrés, et de prendre la moitié de la moyenne de ces carrés. Il n'y a plus alors qu'à voir si la valeur donnée pour N par l'équation d'Einstein

$$\xi^2 = \tau \frac{RT}{N} \frac{1}{5\pi a^2}$$

concorde, dans les limites des erreurs d'expérience, avec la valeur déjà déterminée.

A titre préliminaire, M. Claudesaigues, étudia des grains de gomme-gutte relativement gros; mais assez médiocrement identiques, de rayon à peu près égal à $0,45\mu$. Il nota le déplacement de 40 de ces grains pendant 1 minute, et de 25 pendant 2 minutes; ces pointés donnèrent pour N la valeur $94 \cdot 10^{22}$. D'autre part, 30 grains sensiblement identiques, de rayon un peu supérieur, égal à $0,50\mu$, me donnaient $66 \cdot 10^{22}$, ce qui fait en moyenne $80 \cdot 10^{22}$ pour ce groupe de grains.

M. Claudesaigues étudia ensuite les grains de rayon égal à $0,212\mu$ qui m'avaient permis ma détermination la plus précise de N (n° 24). Les deux Tableaux suivants résument les mesures faites avec deux séries de 50 grains, suivis chacun de 30 en 30 secondes pendant 2 minutes, la viscosité étant 0,011 pour la première série (eau à 17°), et 0,012 pour la seconde :

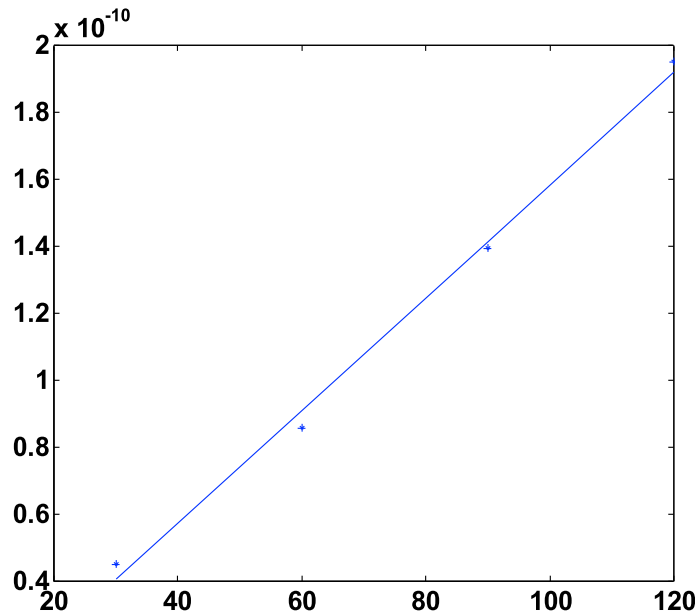
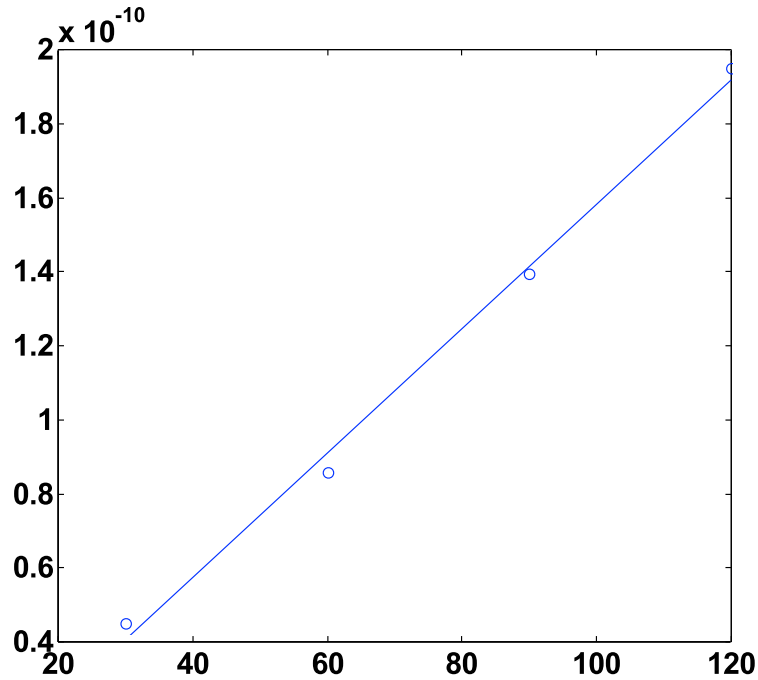
Première série.

DURÉE en secondes.	DÉPLACEMENT horizontal moyen.		N. 10^{22} .	N moyen.
	(en μ).	10^{-4} .		
30	8,9	50,2	66	$73 \cdot 10^{22}$
60	13,4	113,5	59	
90	14,2	128	78	
120	15,2	144	89	

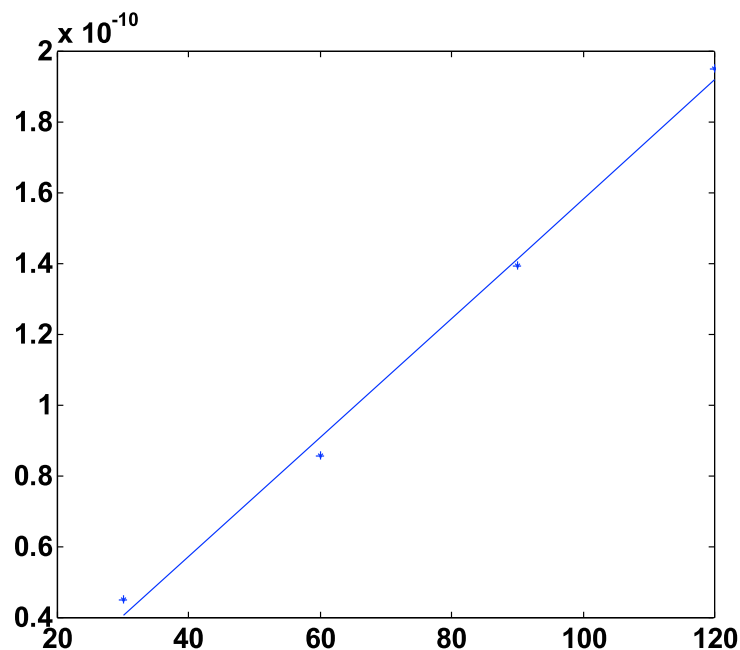
Deuxième série.

30	8,4	45	68	$68 \cdot 10^{22}$
60	11,6	86,5	70,5	
90	14,8	140	71	
120	17,5	195	62	

Enfin, dans une troisième série, toujours avec des grains du même rayon le liquide intergranulaire a été de l'eau fortement sucrée, presque 5 fois plus visqueuse que l'eau pure. Le déplacement moyen en 30 secondes, devenu alors égal à $4,7\mu$, est bien réduit à peu près dans le rapport prévu (à un dixième près) et donne pour N la valeur $56 \cdot 10^{22}$, plus faible que les précédentes, sans pourtant que l'écart dépasse la grandeur qui se trouve possible en raison des



Avogadro number from Brownian motion



Linear fit of the data

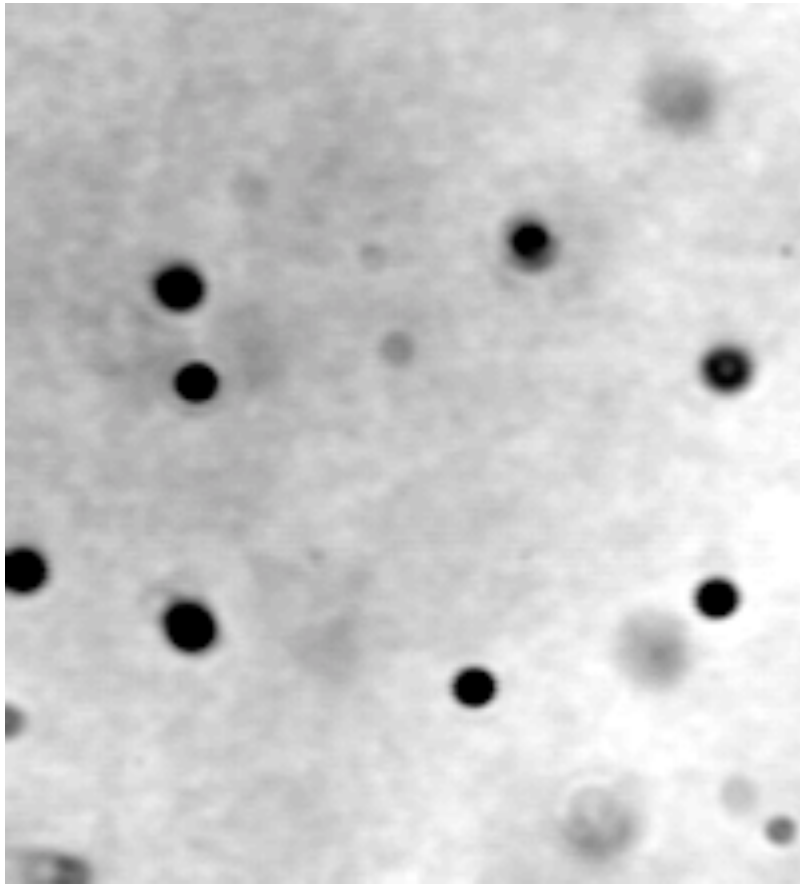
$$\delta x^2 = At + B$$

$$N_A = \frac{RT}{3 A \pi a \eta}$$

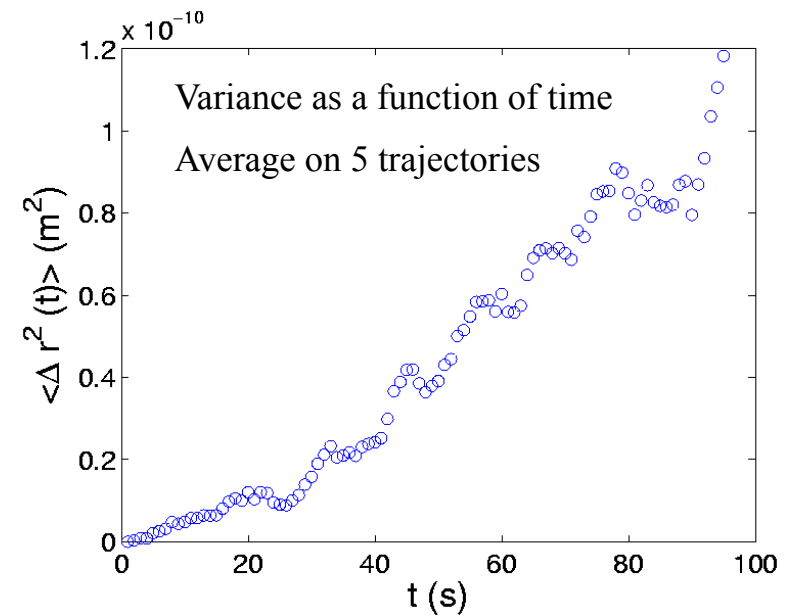
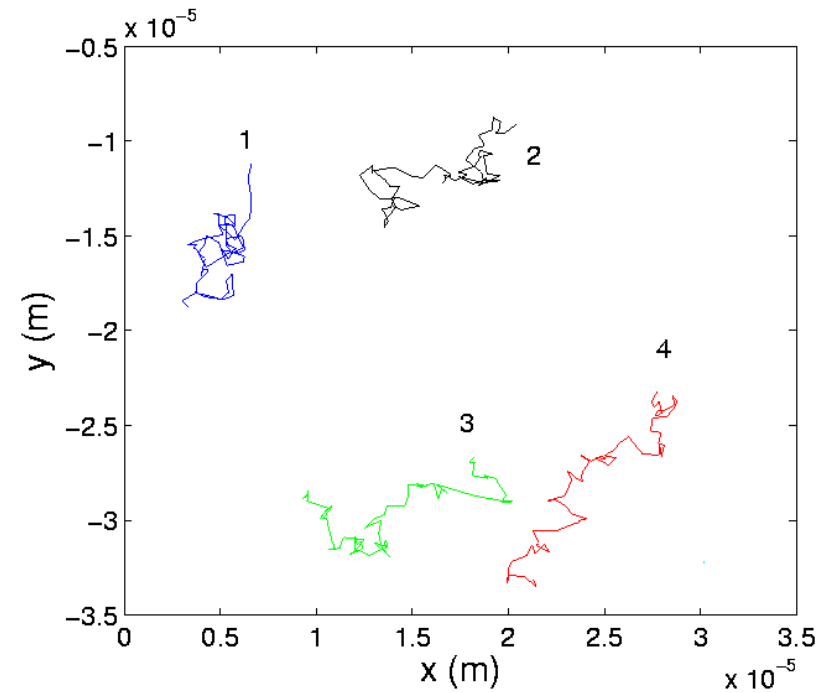
first series $N_A \simeq 6.5 \cdot 10^{23}$

second series $N_A \simeq 6 \cdot 10^{23}$

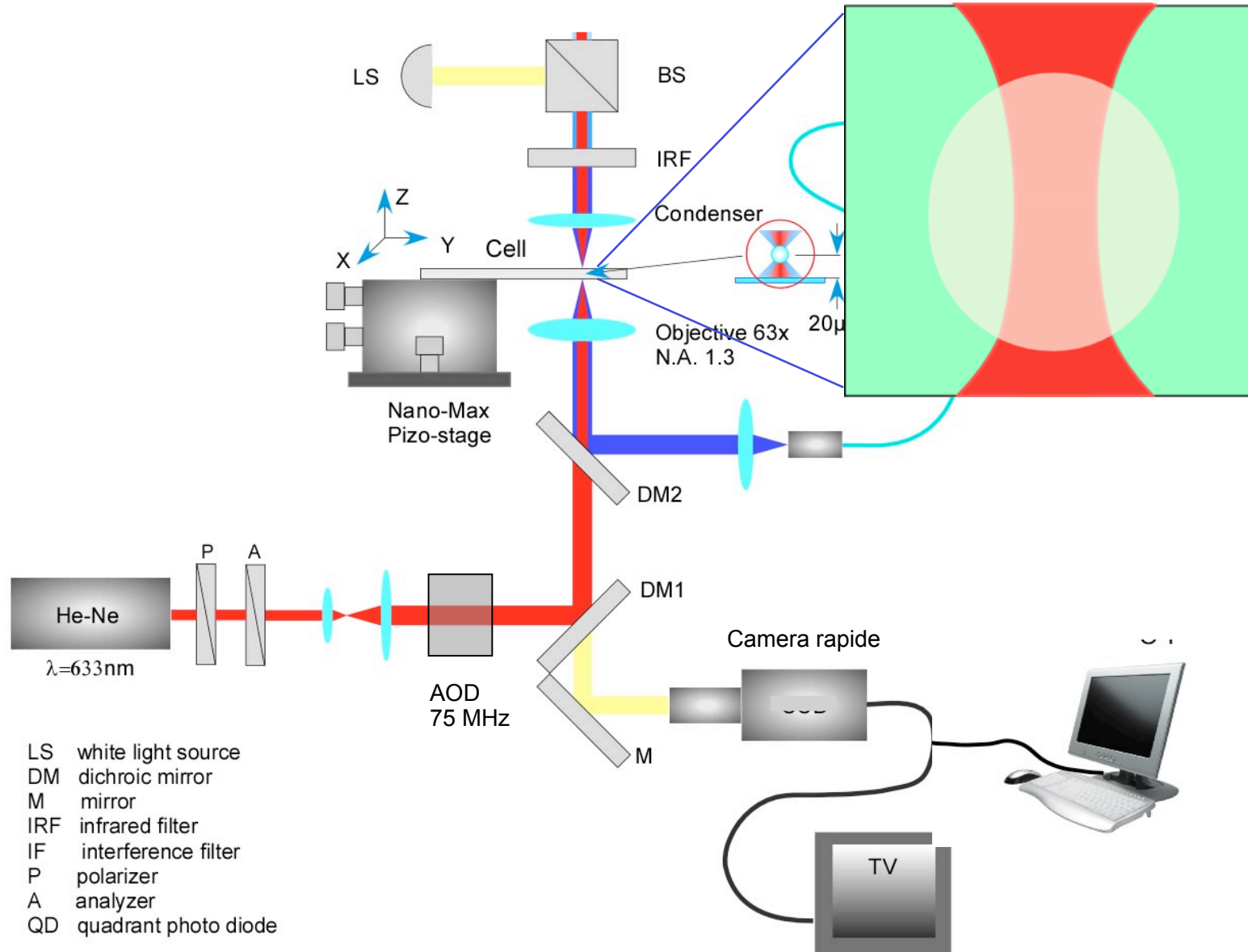
Brownian motion modern measurements



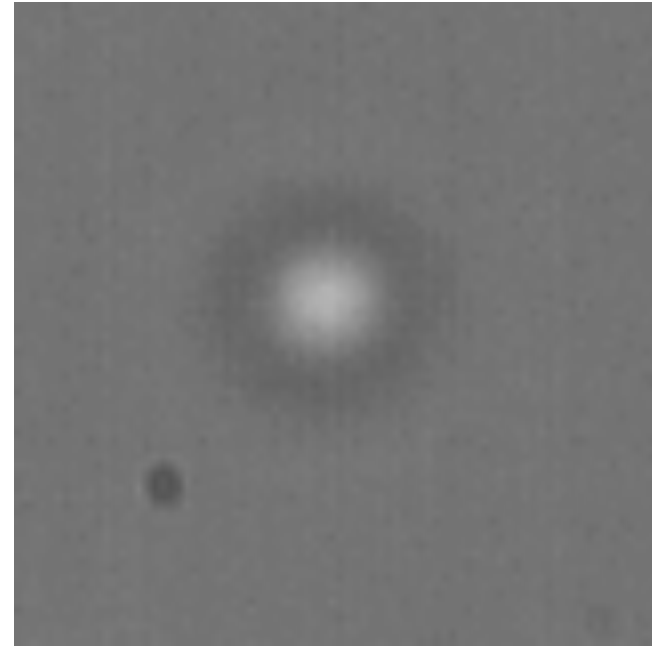
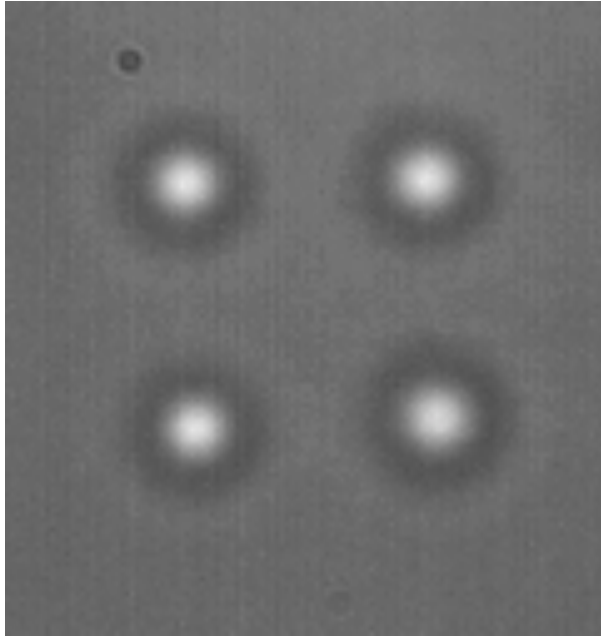
10 times faster than reality



Multiple optical traps



Examples of traps



The Kramer rate is

$$r_k = \tau_o^{-1} \exp\left(-\frac{\delta U}{k_B T}\right)$$

