Marian Smoluchowski

On the Kinetic Theory of the Brownian Molecular Motion and of Suspensions

Annalen der Physik, Band 21, pp. 756–780, 1906
translated from German by R. Schmitz[*] and R. B. Jones[**]

§1. The widely disputed question as to the nature of the phenomena of motion discovered in 1827 by botanist Robert Brown, which occur when microscopically small particles are suspended in fluids, was recently re-addressed in two theoretical papers by Einstein[1]. The conclusions of these papers completely agree with some results that I had obtained a few years ago, following a completely different line of thought, and that I consider ever since to be a substantial argument in favour of the kinetic nature of this phenomenon. Although I was hitherto unable to conduct an experimental investigation on the consequences of this point of view, which I originally intended to do, I have decided after all to publish these ideas now, since thereby I hope to contribute in clarifying this interesting issue, especially since my method seems to me more direct, simpler, and perhaps also more convincing than Einstein's.

To remedy, at least partially, the lack of direct experimental verification, I shall give an overview summarizing the hitherto known experimental results, which, in conjunction with a critical analysis of the different explanation attempts, seem to give clear hints that the Brownian phenomenon is indeed identical to the molecular motions predicted by theory. The paper is concluded by some remarks on suspensions (pseudo-solutions) which are related to the present topic.

[*]Institute for Theoretical Solid State Physics, RWTH Aachen University, Templergraben 55, 52056 Aachen, Germany.
[**]Queen Mary University of London, The School of Physics and Astronomy, Mile End Road, London E1 4NS, UK.

[1]A. Einstein, *Ann. d. Phys.* **17**, p. 549, 1905; **19**, p. 371, 1906.

I

§2. The hitherto existing reports of experiments[2] on Brownian motion mainly prompt negative conclusions, i.e. they exclude various kinds of explanation that are deemed possible at the outset.

The following facts may be considered proven:

The universality of the Brownian phenomenon. – An extraordinary variety of the most diverse substances have been suspended in pulverized form in liquids and examined (especially by Brown, Wiener, Cantoni, Gouy), and in all cases those motions were observed, if only the particles were small enough. Quite the same holds for microscopically small droplets and gas bubbles (e.g. in the cavities of certain minerals that are filled with liquid). Gouy says: "Le point le plus important est la généralité du phénomène; des millers de particules ont été examinées et dans aucun cas on n'a vu une particule en suspension qui n'offrit pas le mouvement habituel…"*

The smaller the diameter s of the particles, the larger is the speed of motion v. For $s > 0.004$mm, motion is barely noticeable, whereas close to the limit of visibility under the microscope it is extremely vivid. Aside from a few crude data by Wiener, it seems that absolute measurements were only performed by Felix Exner, who found for water at 23° temperature:

$s = 0.00013$	0.00009	0.00004cm
$v = 0.00027$	0.00033	0.00038 $\frac{\text{cm}}{\text{sec}}$

Concerning the influence of the composition we find contradicting statements from different observers. Gouy and, similarly, also Jevons claim that particles of fixed size show little speed variation, regardless of what substance they are composed and whether they are solid, liquid or gaseous. On the other hand, Cantoni claims that chemical composition is relevant as well. (Ag is supposed to move faster than Fe, Pt faster than Pb, and the like). Here, it may perhaps play a role that differ-

[2]The sources used here are contained in the following list of references: R. Brown, *Pogg. Ann*. **14**, p. 294, 1828; Cantoni, *Nuovo Cimento* **27**, p. 156, 1867; *Rendic. J. Lomb*. **1**, p. 56, 1868; **22**, p. 152, 1889; Dancer, *Proc. Manch. Soc.* **9**, p. 82, 1869; Felix Exner, *Ann. d. Phys*. **2**, p. 843, 1900; Sigmund Exner, *Wiener Sitzungsber*. **56**, p. 116, 1867; G. Gouy, *Journ. d Phys*. **7**, p. 561, 1888; *Comp. rend*. **109**, p. 102, 1889; Jevons, *Proc. Manch. Soc*. **9**, p. 78, 1869; F. Kolaček, *Beibl*. **13**, p. 877, 1889; K. Maltézos, *Comp. rend*. **121**, p. 303, 1895; *Ann. de chim. et phys*. **1**, p. 559, 1894; Meade Bache, *Proc. Amer. Phil. Soc*. **33**, 1894; *Chem. News* **71**, p. 47, 1895; G. van der Mensbrugghe, *Pogg. Ann*. **138**, p. 323, 1869; Muncke, *Pogg. Ann*. **17**, p. 159, 1829; A. E. Nägeli, *Münch. Sitzungsber*. 1879, p. 389; G. Quincke, *Naturf.-Vers. Düsseldorf* 1898, p. 28; *Beibl*. **23**, p. 934, 1898; E. Raehlmann, *Phys. Zeitschr*. **4**, p. 884, 1903; Regnauld, *Journ. d. pharm*. (3) **34**, p. 141, 1857; Fr. Schultze, *Pogg. Ann*. **129**, p. 366, 1866; W. V. Spring, *Rec. Trav. Chim. Pays-Bas* **19**, p. 204, 1900; O. Wiener, *Pogg. Ann*. **118**, p. 79, 1863.

*"The most important point is the generality of the phenomenon; thousands of particles have been examined and in not a single case has one seen a suspended particle that did not show the usual motion…" [transl. note].

ent substances cannot be pulverized equally well. In any case, the influence of the composition of the particles seems less obvious.

No doubt, however, there is a profound dependence on the nature of the fluid medium, namely on its viscosity: motions are most agile in water and liquids of great fluidity, less in viscous fluids and completely absent in syrup-like fluids, like oil, glycerin, sulfuric acid. They become, however, clearly visible, when glycerin is heated to 50° (S. Exner), whereupon its viscosity decreases considerably. Cantoni states that alcohol, petrol and ether are less active than water, whereas according to Muncke it is alcohol that is most active.

§3. Related to the universality of the phenomenon is its *temporal stability*. Nearly all observers emphasize this fact: as long as the particles are suspended in the liquid, the movement continues without alteration. Only when particles are deposited at the bottom or at the walls of the container do they stop moving. For this reason, it is easier to track, for some time, the motion of particles that have nearly the same density as the ambient liquid (mastic, gamboge) than tracking heavier particles which settle quickly, and, for the same reason (Maltézos, Gouy, Spring), the motion is disrupted by adding saline solution (Jevons), which is well known to cause sedimentation of the particles.

Cantoni observed a specimen, suspended in paraffin oil between cover slips, for a whole year without noticing a diminishing of the movement[3].

§4. Highly characteristic is the *independence* of these phenomena *from external conditions*. The most diverse measures turned out to be without any effect. One may cover the liquid by glass to prevent evaporation (Wiener, Cantoni, Gouy, Exner et. al.), or put it in a heat bath of uniform temperature (Gouy) or place it in a vibration-free location (Exner, Gouy). One may store it for weeks in the dark (Meade Bache), boil it for hours (Maltézos), one may interrupt heat radiation from the incident light, change colour of the light or weaken its intensity by a factor 1000 (Gouy) – all this has no impact.

Intensive illumination causes a change only in that it gradually increases the *temperature* of the fluid, which is associated with an *enhancement of the mobility* (Exner), especially for very viscous fluids in which viscosity strongly decreases with rising temperature. F. Exner has recorded in one case (water) an enhancement from $v = 0.00032$cm/sec at 20° to 0.00051 at 71°.

§5. Concerning the explanation of Brownian motion, it follows mainly from §4 that theories based on *external* energy sources are untenable, thus especially the

[3] Admixture of gelatine hampers the movements, which may be due to the viscosity of gelatine (honeycomb structure, Bütschli). Analogue observations by Quincke may be explained similarly (influence of foam walls).

hypothesis which suggests itself in the first place: that one is dealing here with convective currents caused by temperature inhomogeneities. The untenability of the latter explanation also follows from considerations of a different kind. Thus, motion in water at temperature 4° should completely terminate, whereas, in reality, it continues with only slightly diminished magnitude up to the ice point (Meade Bache). Reduction of the thickness of the fluid layer down to a small fraction of a millimeter by placing a cover glass atop should largely diminish mobility, yet there is no sign of it. A rough estimate shows that, in this case, a temperature gradient in the range of 100000° per cm would be necessary to generate convective currents of the observed velocity. Of course, in larger vessels such currents appear as well, but the collective motions caused by them, which are common to a larger number of particles, are very different from the irregular, jittering Brownian motions.

It should also be noted that the maximal temperature differences near a spherical, completely black particle, which is exposed to direct sun irradiation, amount to a fraction of the coefficient $ca/k = 1/300°$ (assuming: radiation intensity $c = 1/30$, radius $a = 10^{-4}$cm, heat conductivity $k = 10^{-3}$ (water)). Consistent with what has been said above, this may suffice to establish the impossibility of Regnauld's explanation, which is based on the formation of convective currents in the neighbourhood of each particle owing to absorption of radiation at its surface.

The independence of the Brownian phenomenon from light intensity also speaks against the theories of Koláček and Quincke, which respectively take it to be either an analogue of radiometer motion or a manifestation of periodic capillary motions, as analysed by Quincke. In any case, it seems hard to understand how continuous irradiation could cause the periodic propagation of the warmer fluid layers on top of the cooler ones at the surface of the particles, as assumed by Quincke, and how there could possibly be a link between the exceptional phenomenon of periodic capillary motion, which only appears in certain cases (oil in soap solution, alcohol in saline solution etc.), and the universal Brownian motion, which is independent of the composition of the particles. It is, after all, very probable that sufficiently strong irradiation can cause movements, yet these would be very different from the Brownian motion.

§6. There remain only those theories that assume *internal* energy sources. From the outset, we must reject conjectures which assume the existence of mutual repulsion forces (Meade Bache) and related electrical forces (Jevons, Raehlmann), because these could only cause a certain arrangement of the particles, but not their continual motion, and especially because the nature of such forces would constitute a new puzzle.

Also, the view that we are dealing here with manifestations of capillary energy is untenable. Maltézos assumes that small contaminations are the primary cause for the disruption of capillary equilibrium, while Mensbrugghe refers to the example of pieces of camphor dancing on water. But, in this case, it would be inexplicable that deliberate contaminations have no effect, that also completely insoluble substances (diamond, graphite) move and, above all, that motions don't cease when conditions have settled. The microscopically small gas bubbles enclosed in minerals should have reached capillary equilibrium after all, and yet they move.

II

§7. We now turn to the kinetic theories which view the internal heat energy as the real cause. If one observes Brownian motion under the microscope, one immediately gets the impression that the motion of the fluid molecules must look just like that. This is not an oscillatory motion, nor a steady one, but a trembling or, as Gouy puts it, a swarming motion (fourmillement); the particles perform irregular zigzag movements, as if they were driven due to random collisions with the fluid molecules, and despite their feverish motion they only progress slowly from the spot.

This phenomenon was, in fact, explained from this point of view by many researchers (Wiener, Cantoni, Renard, Boussinesq, Gouy). In doing so, two types of interpretation are still possible. Wiener and Gouy assume that, within a region of the order of 1 μ^3, the internal motions of the fluid are aligned and that these are displayed by the particles, whereas Maltézos objected that there is no reason at all to assume parallelism of [fluid] motion within regions of 1 μ^3 and that this hypothesis is not compatible with the independence of these motions at larger separations. We shall come back to these considerations in the sequel, but, for the time being, we shall investigate the simplest kind of kinetic interpretation of this phenomenon, according to which Brownian motion is the immediate result of the momentum transfer from the fluid molecules to the particles.

Nägeli thought to disprove this kind of explanation by referring to the smallness of the velocities caused by such collisions. Thus, a water molecule colliding with a particle of 10^{-4}cm diameter (and density 1) would give it a velocity of just $3 \cdot 10^{-6}$mm/sec, which is far below the scale of Brownian motion. Truly, successive impulses add up, but Nägeli argues that these must cancel on average, since they occur in all spatial directions, and that the final result therefore couldn't be markedly larger [than that for a single collision].

§8. This is the same error in reasoning as if a gambler were to believe that he can never lose an amount of money that is greater than the stake of a single throw. Let us follow this analogy a bit further. Assuming equal probability for gain and loss,