Chapter 1

Introduction

1.1 Fluctuations

In a typical scattering experiment with photons (light), neutrons or electrons a system is bombarded with particles from a source and the scattered particles are collected and analyzed in a detector. A schematic setup for light scattering is shown in fig. 1.1.

The position of the detector defines the scattering angle θ. The structure and dynamics of diverse systems such as solids, liquid crystals, gels, solutions of biological macromolecules, simple molecular fluids, electrolyte solutions, dispersions of microorganisms, solution of viruses, membrane vesicles, protoplasm in algae and colloidal dispersions have been studied by various scattering techniques.

From conservation of momentum and energy we have

$$\boldsymbol{q} = \boldsymbol{k}_i - \boldsymbol{k}_f$$
$$\hbar\omega = E_i - E_f \tag{1.1}$$

where $\boldsymbol{k}_i, E_i$ and $\boldsymbol{k}_f, E_f$ are the wavevectors and energies of the incoming and scattered particles respectively, and $\boldsymbol{q}, \omega$ are wavevector and frequency of excitations in the system. Hence in a scattering experiment we measure the momentum and energy transfer to the fluctuations in the system.

The incident radiation can be described by a plane wave

$$\psi_i(\boldsymbol{r}, t) = \psi_0 \mathrm{e}^{\mathrm{i}(\boldsymbol{k}_i \cdot \boldsymbol{r} - \omega_i t)} \tag{1.2}$$

of wavelength $\lambda_i = 2\pi/k_i$, frequency $\omega_i = E_i/\hbar$ and amplitude ψ_0. Here ψ could be a scalar or a vector field.

The molecules in the scattering region are perpetually translating, rotating and vibrating due to thermal interactions. Because of this motion the positions of the particles and charges in the system are constantly changing so that the scattered field at the detector will fluctuate in time. The scattered field arises from interactions between the molecules in the system and the incoming particles.

Implicit in these fluctuations is important structural and dynamical information about the positions and orientations of the molecules. The thermal molecular motions are erratic, so the scattered field at the detector varies randomly. For example, the intensity of
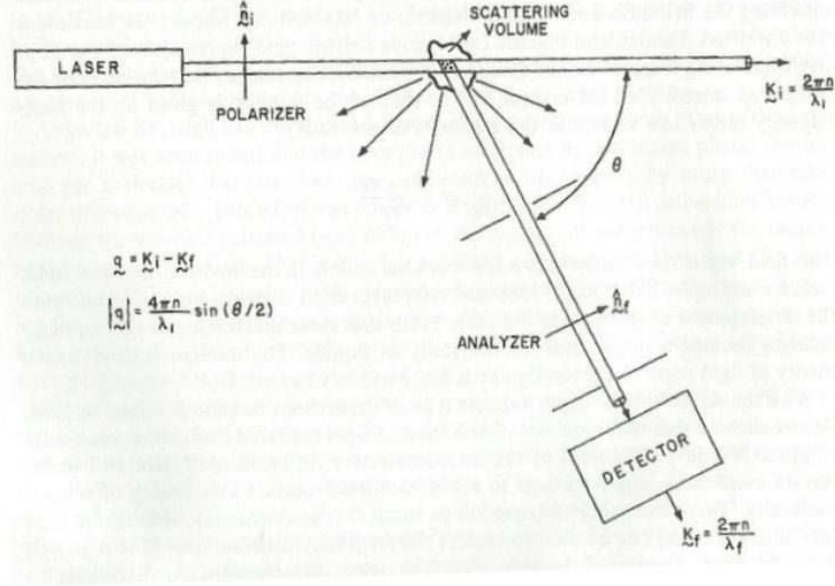
Figure 1.1: *A schematic representation of a light-scattering experiment.*

scattered light from an aqueous solution of polysterene spheres of radius 1.01 μm as a function of time is shown in fig 1.2a. In figure 1.2b we show the timeaveraged autocorrelation function (se below) of the scattered intensity.

Let us consider a property or dynamical variable A that depends on the positions and momenta of all the particles in the system $A(\boldsymbol{r}^N(t), \boldsymbol{p}^N(t))$ where $\boldsymbol{r}^N = \{\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N\}$ and $\boldsymbol{p}^N = \{\boldsymbol{p}_1, \boldsymbol{p}_2, \ldots, \boldsymbol{p}_N\}$. By virtue of their thermal motions the particles are constantly jostling around so that their positions and momenta are changing in time, and so too is the variable A. Although the constituent particles are moving according to Newtons equations (or Schrödingers equation) their very number makes their motion appear to be somewhat random. A typical particle path projected onto the $x - y$-plane is shown in fig. 1.3a. The time dependence of the variable $A(t)$ will also fluctuate and will generally resemble a noise pattern as shown in figure 1.3b.

As an example of a dynamical variable of great importance, consider the local density for the system in a small volume ΔV around a point $\boldsymbol{r}$. Due to the motion of the molecules the number of molecules $N(t)$ in the small volume ΔV will fluctuate. Molecules are constantly entering and leaving the volume and this leads to fluctuations in the local density

$$n(\boldsymbol{r}, t) = \sum_{J=1}^{N} \delta(\boldsymbol{r} - \boldsymbol{r}_j(t)), \quad \boldsymbol{r}_j \in \Delta V$$
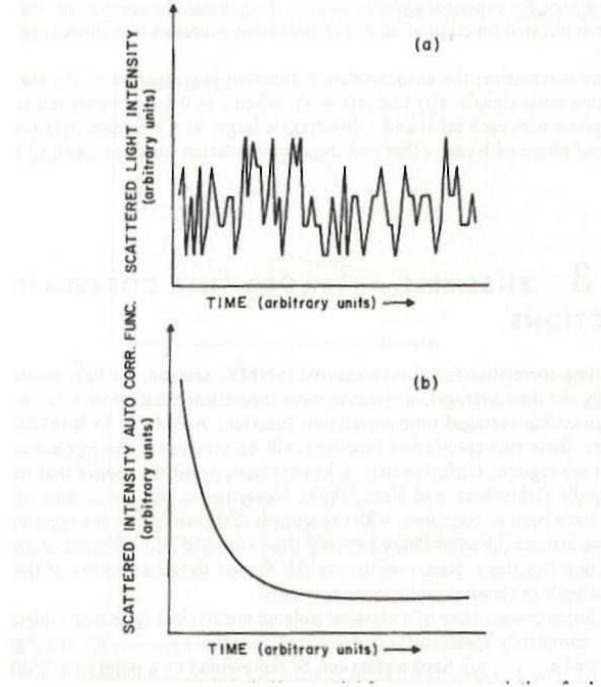
Figure 1.2: *(a) Intensity of scattered light from an aqueous solution of polysterene spheres of radius 1.01 μm as a function of time. (b) The time-averaged autocorrelation function of the scattered intensity in (a) as a function of time.*

The measured bulk property of an equilibrium system is obtained by a time average

$$\overline{A}(t_0, T) = \frac{1}{T} \int_{t_0}^{t_0+T} A(t)\mathrm{d}r \qquad (1.3)$$

where t_0 is the time at which the measurement is initiated and T is the time over which it is averaged. The average becomes meaningful only if T is large compared to the period of fluctuations. The ideal expriment would be one in which A is averaged over an infinite time

$$\overline{A}(t_0, T) = \lim_{T \to \infty} \frac{1}{T} \int_{t_0}^{t_0+T} A(t)\mathrm{d}t \qquad (1.4)$$

Under certain general conditions this infinite average is independent of t_0 for a system in equilibrium. In this case we speak of a *stationary property* and write

$$\langle A \rangle = \lim_{T \to \infty} \frac{1}{T} \int_{0}^{T} A(t)\mathrm{d}t \qquad (1.5)$$

A measure of the fluctuations or correlations in $A(t)$ can be obtained if we consider two times t and $t + \tau$. These values are in general different so that $A(t + \tau) \neq A(t)$. The
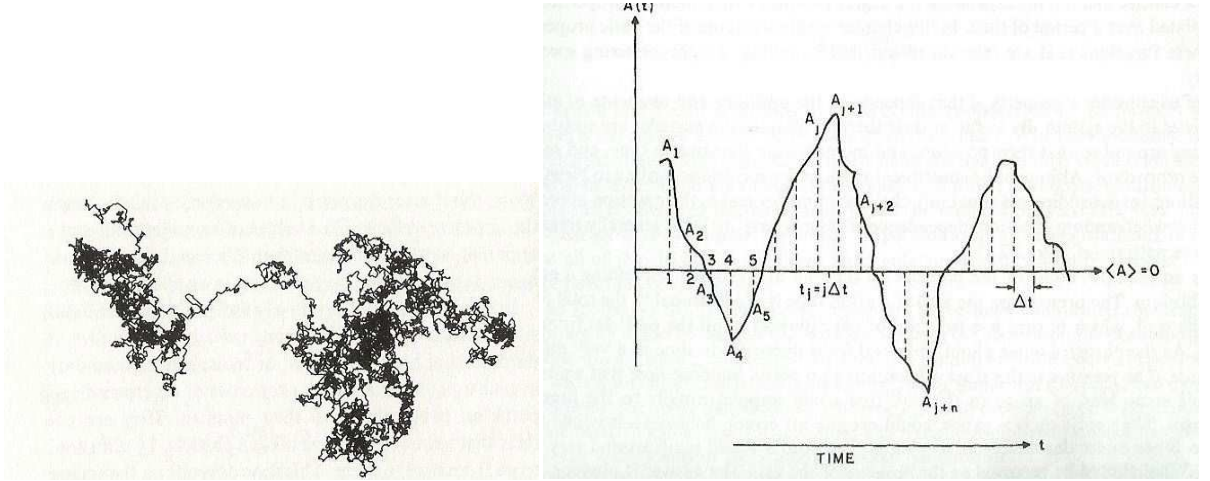
Figure 1.3: *(a) An x, y plot of a two-dimensional random walk of $n = 18050$ steps. The particle repeatedly traversed regions that are completely black. (b) The property $A(t)$ fluctuates in time as the molecules move around in the system. The time axis is divided into discrete intervals Δt, and the time averaged $\langle A \rangle$ is for convenience assumed to be zero.*

autocorrelation function of $A(t)$ is defined by

$$\langle A(0)A(t) \rangle = \lim_{T \to \infty} \frac{1}{T} \int_0^T A(s)A(s+t)\mathrm{d}s \tag{1.6}$$

In an experiment the time axis is usually divided into discrete intervals Δt, such that $s = j\Delta t, t = n\Delta t, T = N\Delta t$ and $s + t = (j + n)\Delta t$. Here Δt should be choosen so small that $A(t)$ varies very little over the time interval Δt. From the definition of the integral it follows that (**??**) and (**??**) can be approximated as

$$\langle A \rangle \quad \approx \quad \lim_{N \to \infty} \frac{1}{N} \sum_{j=1}^{N} A_j$$

$$\langle A(0)A(t) \rangle \quad \approx \quad \lim_{N \to \infty} \frac{1}{N} \sum_{J=1}^{N} A_j A_{j+n} \tag{1.7}$$

In experiments a correlator computes time-correlation functions of the scattered field in this discrete manner, as indicated in fig. 1.3b.

1.2   Correlation functions

For a system close to thermodynamic equilibrium the average value and the correlation function in (**??**) and (**??**) contain all relevant information of the system. If we perturb the system slightly out of equilibrium and follow the systems relaxation back towards equilibrium we find

$$\langle A(t) \rangle_{\mathrm{neq}} = C_{AA}(t)/C_{AA}(0)\langle A(0) \rangle_{\mathrm{neq}} \tag{1.8}$$

where $C_{AA}(t) = \langle A(0)A(t) \rangle_{\text{eq}}$ is the autocorrelation function for the equilibrium system. What we want to find out is how the time correlation varies with time.

From the Schwartz inequality

$$\left| \sum_j A_j B_j \right|^2 \leq \left(\sum_j A_j^2 \right) \left(\sum_j B_j^2 \right) \tag{1.9}$$

it follows with $B_j = A_{j+n}$ that

$$\langle A(0)A(t) \rangle \leq \langle A^2(0) \rangle \tag{1.10}$$

Thus the autocorrelation function either remains equal to its initial value or decays with time. For times τ large compared to the characteristic time for the fluctuations of A, $A(t)$ and $A(t + \tau)$ are expected to become totally uncorrelated i.e.

$$\lim_{\tau \to \infty} \langle A(0)A(\tau) \rangle = \langle A(0) \rangle \langle A(\tau) \rangle = \langle A \rangle^2 \tag{1.11}$$

so that the time correlation function decays from $\langle A^2 \rangle$ to $\langle A \rangle^2$ in the course of time. In many applications the autocorrelation function decays like a single expoonential so that

$$\langle A(0)A(t) = \langle A \rangle^2 + \left(\langle A^2 \rangle - \langle A \rangle^2 \right) e^{-t/\tau_{\text{R}}} \tag{1.12}$$

where τ_{R} is called the relaxation time or the correlation time of the property. It represents the characteristic decay time of the property. If we define

$$\delta A = A - \langle A \rangle \tag{1.13}$$

which is the definition of the instantaneous value of $A(t)$ from its average we can write (??) as

$$\langle \delta A(0)\delta A(t) \rangle = \langle \delta A^2 \rangle e^{-t/\tau_{\text{R}}} \tag{1.14}$$

1.3   Calculation of correlation functions

The time correlation functions measured in NMR, neutron and light-scattering spectroscopy are time averages as described above, Most theoretical calculations calculate the ensemble-averaged time-correlation function. According to Birkhoff's ergodic theorem, these two correlation functions will be identical if the mechanical system studied is ergodic.

The *instantaneous state* of a classical isolated mechanical system of f degrees of freedom is completely specified by f generalized positions $(q_1, \ldots, q_f)$ and f generalized momenta $(p_1, \ldots, p_f)$. These can be the ordinary positions and momenta $(q_1, \ldots, q_f) = (r_{1x}, \ldots, r_{Nz})$ etc with $f = 3N$ or some other suitable coordinates. A state is represented by a point in a $2f$ dimensional cartesian space with orthogonal coordinate axes labeled by these f positions and f momenta. Given the initial state $\Gamma_0 = (q_1(0), \ldots, p_f(0))$ the canonical equations of motion

$$\begin{aligned} \dot{q}_i &= \frac{\partial H}{\partial p_i} \\ \dot{p}_i &= -\frac{\partial H}{\partial q_i}, \qquad i = 1, \ldots, f \end{aligned} \tag{1.15}$$

have unique solutions so that all subsequent states of the system are unambigously specified for all time. This means that as time goes by the particles move to new positions with new momenta. The specific positions and momenta at any time t, $\Gamma_t = (q_1(t), \ldots, p_f(t))$ are totally determined by the initial state of the system and the canonical equations, with the Hamiltonian

$$H = T(p_1, \ldots, p_f) + V(q_1, \ldots, q_f) \tag{1.16}$$

where T is the kinetic and V is the potential energy of the particles. The complete behaviour of the system can be represented by a trajectory i phase-space as shown in fig 1.4a. A dynamical variable is a function of the instantaneous state Γ_t of the system. For the variable A we then have $A(t) = A(\Gamma_t)$. As time goes by a property will change unless it is a constant of the motion. The typical behaviour of a property A corresponding to a given trajectory in phase space is illustarted in fig. 1.4b. From the canonical equations of motion (**??**) one readily obtains the equation of motion

$$\frac{\mathrm{d}A(t)}{\mathrm{d}t} = \sum_{i=1}^{f} \left(\frac{\partial A}{\partial q_i} \dot{q}_i + \frac{\partial A}{\partial p_i} \dot{p}_i \right) = \sum_{i=1}^{f} \left(\frac{\partial A}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial A}{\partial p_i} \frac{\partial H}{\partial q_i} \right) = [A(t), H]_{\mathrm{PB}} = -\mathrm{i}\mathcal{L}A(t) \tag{1.17}$$

where $[.., ..]_{\mathrm{PB}}$ denotes the Poisson-bracket and $\mathcal{L}$ is the Liouville operator. Here we have assumed that the time dependence of A only enters via the dependence on the time dependence of the phanse-space variables Γ_t.

The classical equilibrium ensemble-averaged time correlation function of the property A is defined as

$$\langle A(0)A(t) \rangle = \int \mathrm{d}\Gamma_0 \rho(\Gamma_0) A(\Gamma_0) A(\Gamma_t) \tag{1.18}$$

where $\rho(\Gamma_0)\mathrm{d}\Gamma_0$ is the probability of finding the system in the initial state Γ_0. For example in the canonical equilibrium ensemble we have

$$\rho(\Gamma_0) = \frac{1}{Z} \mathrm{e}^{-\beta H(\Gamma_0)}, \quad Z = \int \mathrm{d}\Gamma_0 \mathrm{e}^{-\beta H_0} \tag{1.19}$$

with $\beta = 1/k_{\mathrm{B}}T$ where k_{B} is Boltzmanns constant and T the temperature.

In quantum statistical mechanics the time-correlation function of the observable A is defined as

$$\langle A(0)A(t) \rangle = \mathrm{Tr}\rho_0 A \mathrm{e}^{\mathrm{i}Ht/\hbar} A \mathrm{e}^{-\mathrm{i}Ht/\hbar} \tag{1.20}$$

where ρ_0 is the equilibrium density matrix, A is the Hermitian operator representing the observable A, H is the Hamiltonian operator and $A(t) = \mathrm{e}^{\mathrm{i}Ht/\hbar} A \mathrm{e}^{-\mathrm{i}Ht/\hbar}$ is the operator representing the observable A at time t in the Heisenberg representation. Taking the time-derivative of $A(t)$ we find

$$\mathrm{i}\hbar \frac{\mathrm{d}A(t)}{\mathrm{d}t} = [A(t), H] = -\mathrm{i}\mathcal{L}A(t) \tag{1.21}$$

where $[.., ..]$ denotes the commutator and $\mathcal{L}$ the quantum mechanical Liuoville operator.

Equations (**??**) and (**??**) give together with the canonical equations of motion (**??**) and (**??**) well defined prescriptions to calculate time-correlation functions, and except for the average over an stationary ensemble there is no stochastic ingredient in these equations.
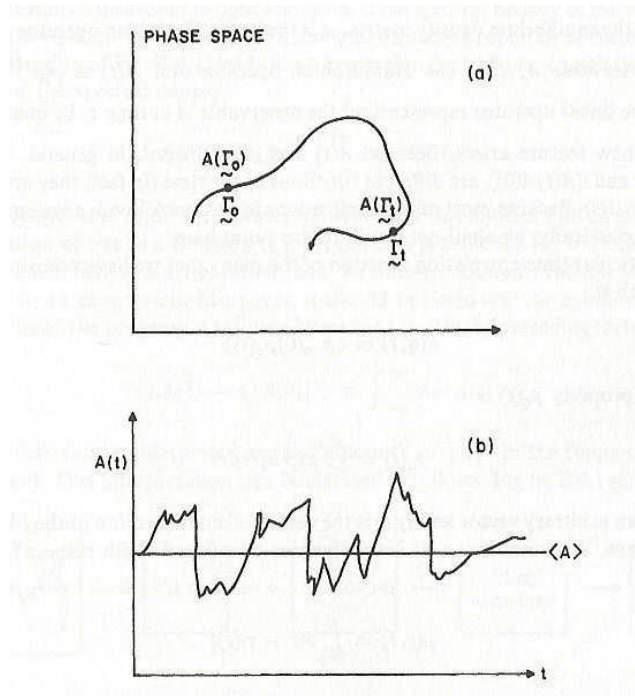
Figure 1.4: *(a) Schematic representation of a trajectory in phase space. Γ_0 and Γ_t represent the states of the system at time 0 and t. (b) The variation of the mechanical property A with respect to time corresponding to the trajectory in (a).*

In practice, however, the microsacopic equations are to complex to solve for many systems in nature. A simplified description with stochastic equations of motion is therefore often applied. This means that we replace the Liouville oparator in the microscopic equations with some stochastic operator $\mathcal{L}_S$

$$\frac{\mathrm{d}A(t)}{\mathrm{d}t} = -\mathrm{i}\mathcal{L}_S A(t).$$

Still however correlation functions are defined as in (**??**) and (**??**) provided that $A(t)$ is obtained as a solution of the model equation above.

1.4 Brownian motion

One of the first observations of stochastic motion in physics was made by Robert Brown in 1827, who observed the motion of pollen grains dissolved in water. A short history of these studies is given below.

> In the year 1803, Napoleon sold France's North American colonies to that new nation, the United States, for the small sum of sixty million francs. This sale is known in American history books as the Louisiana Purchase. President Thomas Jefferson, wishing to find out exactly what he had bought, sent out an expedition of exploration
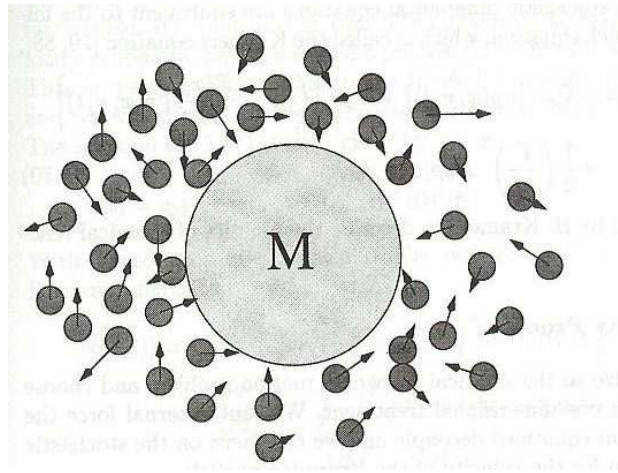
Figure 1.5: *A large Brownian particle with mass M immersed in a fluid of much smaller and lighter particles.*

under the leadership of Meriweather Lewis and William Clark. Among the contributions of the Lewis and Clark expedition, one of the least significant would have the greatest impact, albeit indirectly, on physics and chemistry.

The Lewis and Clark expedition left in 1804, reached the Pacific Ocean in November 1805, and returned in 1806. The story of the expedition, based on Lewis' and Clark's journals, makes a marvelous adventure story. In addition to geographical and ethnographical information, the expedition also brought back botanical specimens. A genus of plants from among these specimens was named after Captain William Clark. One member of this genus was Clarkia pulchella, a wildflower found in the Pacific Northwest of the United States.

Specimens of Clarkia pulchella were brought to England in 1826 by the Scots botanist David Douglas, who made an expedition to the Pacific Northwest in the years 1824-1828. It is he after whom the magnificent Douglas fir (pseudotsuga menziesii) is named.

By the year 1827, Robert Brown (1773-1858) was a renowned botanist. As a young man, Brown studied medicine at Edinburgh, but never finished his studies nor took a degree. He enlisted in a newly raised Scottish regiment and was posted to Ireland, where he was appointed Surgeon's Mate, although he seems to have spent more time collecting botanical specimens than attending to patients.

Brown acquired some reputation as a botanist, and had come to the attention of Sir Joseph Banks who was organizing an expedition to Australia, or, as it was then called, New Holland. Banks had need of a botanist for the expedition, and offered the position to Brown. Brown's medical experience no doubt weighed in his favor. Robert Brown accepted as soon as he could sever his connection with the army, and his formal career as a botanist was begun.

In addition to collecting and c1assifying, Brown made several important discoveries in botany. Perhaps the one most celebrated by biologists is his discovery that plant cells are eukaryotic, that they have a nucleus. Among physical scientists and mathematicians, however, he is known primarily for the eponymous motion associated with his name

In 1827, Brown was investigating the way in which pollen acted during impreg-

nation. He wanted to use non-spherical grains, in order to be able to observe their orientation. The first plant he studied under the microscope was Clarkia pulchella, whose polIen contains granules varying from about five to six microns in linear dimension. It is these granules, not the whole pollen grains, upon which Brown made his observations. Concerning them, he wrote

> *While examining the form of these particles immersed in water, I observed many of them very evidently in motion... These motions were such as to satisfy me, after frequently repeated observation, that they arose neither from currents in the Fluid, nor from its gradual evaporation, but belonged to the partic1e itself.(Brown 1828)*

This inherent, incessant motion of small partic1es suspended in a fluid is nowadays called Brownian motion in honor of Robert Brown. In fig. 1.5 a sherical particle immersed in a fluid of smaller particles is shown. Similar observations had, in fact, been made earlier by other workers. Brown, however, was the first to give them serious scientific study, and to show that, in fact, they were not due to the living origin of the moving partic1es. It can be said that Brown, the botanist, showed that the phenomenon was not one of biology, but one of physics.

For example, Brown had strongly illuminated the specimens under his microscope and hence had heated them. This caused evaporation of the ambient fluid, and Brown asked whether this evaporation might be causing the motion which he observed. To answer this experimentally, he made a mixture of water containing particles with an immiscible oil and shook the mixture until small drops of water were formed in the oil, some containing only a single particle. These were stable and did not evaporate for some time. He wrote

> *But in all the drops thus formed and protected, the motion of the particles takes place with undiminished activity, while the principal causes assigned for that motion, namely, evaporation, and their mutual attraction and repulsion, are either materially reduced, or absolutely nil.*

Brown had his results printed in a parnphlet, entitled "A briel account of microscopical observations made in the months of June, July, and August, 1827 on the particles contained in the pollen of plants; and on the general existence of active molecules in organic and inorganic bodies". This work was originally intended for private circulation, but was reprinted in the archival literature shortly after its appearance (Brown 1828). Brown used the word molecule in the title in a sense different from its current one. It referred to earlier teaching of the Comte de Buffon (1707-1786) who introduced ths word for the ultmate constituents of the bodies of living beings. This had nothing to do with the later development of Dalton's atomic theory in which the word molecule took on its modern meaning.

Brown published a second paper on the motion (Brown 1829). In it he reported the experiments on the oil-water emulsion mentioned above, and discussed previous observations by others which could have been interpreted as prior to his. He claimed that these previous observations were of motile animalcules or organisms. In one case in which an author claimed to have observed animated inorganic particles, Brown states that the observation is suspect because the author was susceptible to 'optical illusions'.

There was, however, one predecessor whom Brown overlooked. In July of 1784, Jan Ingen-Housz published a short paper entitled "Remarks on the use of the microscope" (Ingen-Housz 1789) that contains the following lines
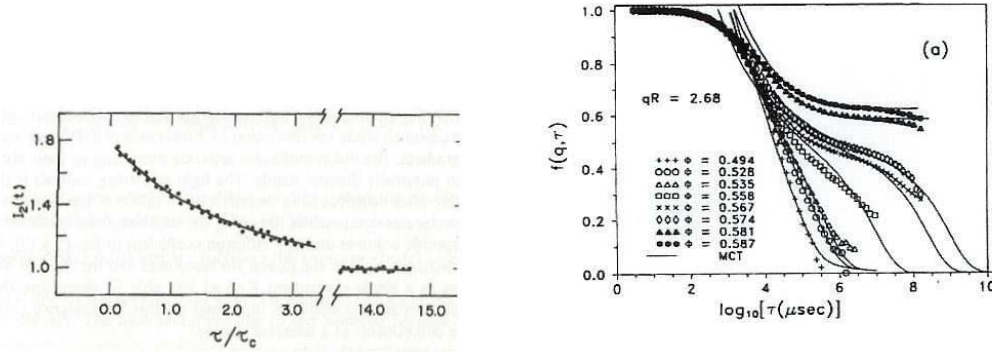
Figure 1.6: *(Left) Correlation function obtained with light scattering at a scattering angle of 60° for a solution containing 0.17 mg/cm^3 of fd DNA in SCC (0.15 m NaCl, 0.015 m Nacitrate, pH=8) as a function of $\tau/$ where $\tau_c = (q^2 D)^{-1}$ is the correlation time. (Right) Scattering function for colloidal spheres at various densities ranging from $\Phi = 0.494$ to $\Phi = 0.587$.*

> ...one must agree that, as long as the droplet lasts, the entire liquid and conse-
> quently everything which is contained in it, is kept in continuous motion by the evap-
> oration, and that this motion can give the impression that some of the corpuscles are
> living, even if they have not the slightest life in them. To see clearly how one can
> deceive one's mind on this point if one is not careful; one has only to place a drop of
> alcohol at the focal point of a microscope and introduce a little finely ground charcoal
> therein, and one will see these corpuscles in a confused continuous and violent motion
> as if tbey were animalcules which move violently around.
>
> On the basis o these few lines, Van der Pas (1971) has argued that Ingen-Housz
> should be accorded priority in the discovery of Brownian motion. However, although
> Ingen-Housz doubtless observed the motion, he did not follow up his observation with
> any investigation of it, as did Brown. His ascription of the motion to evaporation was,
> as Brown showed in a simple experiment, quite wrong. Robert Brown still deserves
> pride of place with respect to the discovery of the motion now named after him.

It took about 80 years until Einstein and Smoluchowski gave a theoretical explanation of the phenomenon. Today the study of the dynamics of colloidal solutions are still of high interest. In particular colloids are used as model systems to study glass transition and gelation.

One of the difficulties in colloids is that there are three different time scales:

$$\tau_c \ll \tau_{\mathrm{B}} \leq \tau_{\mathrm{R}}$$

Here $\tau_c \approx 10^{-12}$ s is a typical collision time of the small liquid particles, $\tau_{\mathrm{B}} = M/\zeta$ is the Brownian relaxation time for the velocity of the Brownian particle, and $\tau_{\mathrm{R}} = R^2/D$ is the relaxation time for the displacement of the Brownian particle. Here M is the mass of the Brownian particle, $\zeta = 6\pi\eta R$ is a friction coefficient given by the solvent viscosity η and the radius of the Brownian particle, and D is the diffusion coefficient of the Brownian particle. A typical calue of τ_{B} is 10^{-3} s. For dilute solutions $\tau_{\mathrm{B}} \approx \tau_{\mathrm{R}}$ while when the
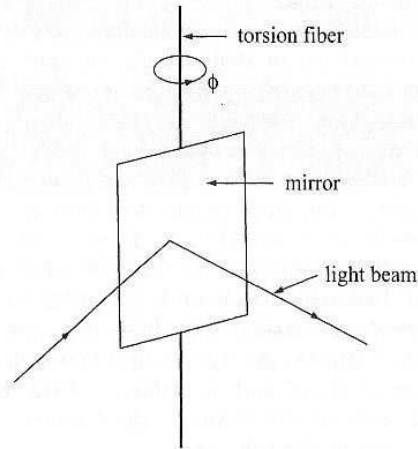
Figure 1.7: *The reflection of a light beam from a mirror mounted on a torsion fiber.*

density of Brownian particles increase the diffusion coefficient rapidly decreases and for such systems $\tau_{\mathrm{B}} \ll \tau_{\mathrm{R}}$.

Since it is very difficult to handle this large separation of time-scales the microscopic Liouville equation cannot be used to study colloids, but a stochastic model is necessary.

In fig. 1.6 we show light scattering measurements of the density correlation function for dilute and dense colloidal solutions. When the density increase one finds a rapid slowing down of the motion i.e. τ_{R} rapidly increases.

A relatively early application of Brownian motion was made by Perrin and others to measure Avogadros number. A small mirror is mounted on a fiber, as depicted in fig. 1.7. The fiber and its associated mirror is suspended in a gas; this may be the ambient air or it may be the residual gas in an evacuated chamber. Consequently the mirror will be constantly bombarded by gas molecules, and undergo a rotational Brownian motion. The resulting torque causes the fiber to rotate through an angle ϕ about its axis. The angle of twist is very small, but is magnified many times when a beam of light is reflected from the mirror when the light path between the mirror and the measuring scale is long enough.

For small angles of twist, the potential energy of the twist is assumed to be

$$V(\phi) = \frac{1}{2}b\phi^2$$

where b is the torsional constant of the fiber. The system has one degree of freedom.

The fluctuations of the angle ϕ is a measure of the precision of the measurement. From the equipartition theorem alone, without anything more complicated, the mean.square fluctuation in the angle ϕ can immediately be writte as

$$\frac{1}{2}b\langle\phi^2\rangle = \frac{1}{2}k_{\mathrm{B}}T$$
$$\langle\phi^2\rangle = \frac{k_{\mathrm{B}}T}{b}$$

Test of this result was carried out by Perrin and later by Gerlach and Lehrer in order to accurately determine Avogadro's number $N_{\mathrm{A}} = R/k_{\mathrm{B}}$ with R being the universal gas
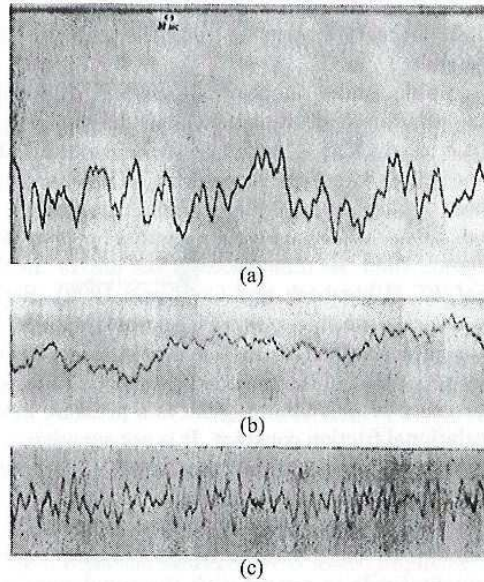
Figure 1.8: *Some of the results of Kappler's measurements of the Brownian motion of a mirror mounted on a torsion fibre. Traces (a) and (c) have similar pressures (4×10^{-3} torr and 1×10^{-3} torr respectively), but different mechanical properties. Traces (b) and (c) have the same mechanical propereties but (b) is at atmospheric pressure.*

connstant. It was one of the first findings where the consideration of fluctuations gave a strong support to prove the molecular structure of matter.

Kappler repeated these measurements with pressures ranging from 10^{-4} mm of Hg to 1 atm. The mean-square torsion was independent of pressure, but the qualitative appearence of the oscillating fluctuations was considerably affected by the pressure of the experimental run. Examples are shown in fig. 1.8.