

100 years of Einstein's Theory of Brownian Motion: from Pollen Grains to Protein Trains – 1.

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Experimental verification of the theoretical predictions made by Albert Einstein in his paper, published in 1905, on the molecular mechanisms of Brownian motion established the existence of atoms. In the last 100 years Brownian motion has not only revolutionized our fundamental understanding of the nature of *thermal fluctuations* in physical systems, but it has also explained many counterintuitive phenomena in earth and environmental sciences as well as in life sciences. This 2-part article begins with a brief historical survey and an introduction to the concepts and theoretical techniques for studying Brownian motion. Then, in *Part 2* a discussion on rotational Brownian motion and Brownian shape fluctuations of soft materials is followed by an elementary introduction to two of the hottest topics in this contemporary area of interdisciplinary research, namely, *stochastic resonance* and *Brownian ratchet*.

1. Introduction

The United Nations has declared the year 2005 as the 'World Year of Physics' to commemorate the publication of the three papers of Albert Einstein in 1905 on (i) special theory of relativity, (ii) photoelectric effect and (iii) Brownian motion [1]. These three papers not only revolutionized physics but also provided keys to open new frontiers in other branches of science and almost all areas of modern technology. In one of these three papers [2], entitled "On the movement of small particles suspended in a stationary liquid demanded by the molecular kinetic theory of heat", Einstein developed a quantitative the-



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Keywords

Brownian motion, Langevin equation, fluctuation-dissipation.



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ory of Brownian motion assuming an underlying molecular mechanism. Popular science writers have written very little on this revolutionary contribution of Einstein; most of the media attention was attracted by his theory of relativity although he received the Nobel Prize for his theory of photoelectric effect which strengthened the foundation of quantum theory laid down somewhat earlier by Max Planck. Is Brownian motion, in any sense, less important than its two more glamorous cousins, namely relativity and quantum phenomena?

Based on the progress of science and technology over the last 100 years we can assert that Brownian motion plays an important role not only in a wide variety of systems studied within the traditional disciplinary boundaries of physical sciences but also in systems that are subjects of investigation in earth and environmental sciences, life sciences as well as in engineering and technology. Some examples of these systems and phenomena will be given in this article. However the greatest importance of Einstein's theory of Brownian motion lies in the fact that experimental verification of his theory silenced all skeptics who did not believe in the existence of atoms.

Didn't people believe in the existence of atoms till 1905? Well, Greek philosophers like, for example, Democritus and Leucippus assumed discrete constituents of matter [3], John Dalton postulated the existence of atoms and, by the end of the nineteenth century a molecular kinetic theory of gases was developed by Clausius, Maxwell and Boltzmann. Yet, the existence of atoms and molecules was not universally accepted. For example, physicist-philosopher Ernst Mach believed that atoms have only a didactic utility, i.e., they are useful only in deriving experimentally observable results while they themselves are purely fictitious.

The continuing debate of that period regarding the existence of atoms has been beautifully summarized in the



following words by Jacob Bronowski in his *Ascent of Man* [4]: “Who could think that, only in 1900, peoples were battling, one might say to the death, over the issue whether atoms are real or not. The great philosopher Ernst Mach in Vienna said, NO. The great chemist Wilhelm Ostwald said, NO. And yet one man, at that critical turn of the century, stood up for the reality of atoms on fundamental grounds of theory. He was Ludwig Boltzmann... The ascent of man teetered on a fine intellectual balance at that point, because had the anti-atomic doctrines then really won the day, our advance would certainly have been set back by decades, and perhaps a hundred years.” Therefore, one must not underestimate the importance of Einstein’s paper in 1905 on the theory of Brownian motion as it provided a testing ground for the validity of the molecular kinetic theory. It is an irony of fate that, just when atomic doctrine was on the verge of intellectual victory, Ludwig Boltzmann felt defeated and committed suicide in 1906.

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2. Period Before Einstein

In 1828 Robert Brown, a famous nineteenth century Botanist, published “a brief account of the microscopical observations made in the months of June, July and August, 1827 on the particles contained in the pollen of plants”. Could the incessant random motion of the particles that he observed under his microscope be a consequence of the fact that the pollens were collected from living plants? Naturally, he “was led next to inquire whether this property continued after the death of the plant, and for what length of time it was retained.” He repeated his experiments with particles derived not only from dead plants but also from “rocks of all ages,...a fragment of the Sphinx...volcanic ashes, and meteorites from various localities”. From these experiments he concluded, “extremely minute particles of solid matter, whether obtained from organic or inorganic substances, when suspended in pure water, or in some other

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By the time he completed these investigations, he no longer believed the random motions to be signatures of life. Following Brown’s work, several other investigators studied Brownian motion in further detail. All these investigations helped in narrowing down the plausible cause(s) of the incessant motion of the Brownian particles. For example, temperature gradients, capillary actions, convection currents, etc. could be ruled out.

In the second half of the nineteenth century, Giovanni Cantoni, Joseph Delsaulx and Ignace Carbonelle independently speculated that the random motion of the Brownian particles was caused by collisions with the molecules of the liquid. However, Carl von Nägeli and William Ramsey argued against this possibility. Their arguments were based on the assumption that the particle suffered no collision along a linear segment of its trajectory except those with two fluid particles at the two ends of the segment. If this scenario is true, then, it leads to two puzzles: (i) how can molecules of water, which are so small compared to the pollen grain, cause movements of the latter that are large enough to be visible under an ordinary nineteenth century microscope? (ii) A molecule collides over 10^{12} times per second. On the other hand, our eyes can resolve events that are separated in time by more than $1/30$ second. Therefore, if each displacement of the pollen grain is caused by a single collision with a water molecule, then each such displacement would occur at time intervals of 10^{-12} seconds. But, then, how do our eyes resolve these events and see them as distinct random displacements of the pollen grain? On the basis of these arguments Nägeli and Ramsey tried to rule out the mechanism based on molecular collisions. We shall see how this paradox was resolved later by Smoluchowski, a contemporary of Einstein.



Did Brown really discover the phenomenon which is named after him? No. In fact, Brown himself did not claim to have discovered it. On the contrary, he wrote “the facts ascertained respecting the motion of the particles of the pollen were never considered by me as wholly original...”. Brownian motion had been observed as early as in the seventeenth century by Antony van Leeuwenhoek under simple optical microscope. It was reported by Jan Ingenhousz in the eighteenth century. In fact, Brown himself critically reviewed the works of several of his predecessors and contemporaries on Brownian motion. Over the next three quarters of the nineteenth century, many investigators studied this phenomenon and speculated on the possible underlying mechanisms, major contributors being Guoy and Exner. Nevertheless, this phenomenon was named after Brown; this reminds us of Stiglers law of eponymy: “No scientific discovery is named after its original discoverer”.

Einstein and the Theory of Brownian Motion

For the sake of simplicity, we shall write all the equations for Brownian motion in one-dimensional space; generalizations to higher dimensions is quite straightforward.

Einstein

Einstein published five papers *before 1905* [5]. All of these five papers were, in Kuhn’s terminology, “normal science”. However, the last three of these, which were attempts to address some fundamental questions on the molecular-kinetic approach to thermal physics, prepared him for the “scientific revolution” he created through his paper of 1905 on Brownian motion [2]. The title of that paper, “On the movement of small particles suspended in a stationary liquid demanded by the molecular kinetic theory of heat”, did not even mention Brownian motion !! Einstein was aware of the possible relevance of his theory in Brownian motion but was cautious. He

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“it is possible that the movements to be discussed here are identical with the so-called Brownian molecular motion; however, the information available to me regarding the latter is so lacking in precision, that I can form no judgment in the matter”.

Einstein formulated the problem as follows: “We must assume that the suspended particles perform an irregular movement- even if a very slow one- in the liquid, on account of the molecular movement of the liquid”. This is, indeed, a clearly stated assumption regarding the mechanism of the irregular movement.

The main result of Einstein’s paper of 1905 on Brownian motion can be summarized as follows: the mean-square displacement $\langle x^2 \rangle$ suffered by a spherical Brownian particle, of radius a , in time t is given by

$$\langle x^2 \rangle = \left(\frac{RT}{3\pi N_{av} a \eta} \right) t, \quad (1)$$

where T is the temperature, η is the viscosity of the fluid, R is the gas constant and N_{av} is the Avogadro number. Since $\langle x^2 \rangle$, t , a and η are measurable quantities, the Avogadro number can be determined by using (1).

Einstein had clear idea of the orders of magnitude that would make the movements visible under a microscope. He wrote, “In this paper it will be shown that according to the molecular-kinetic theory of heat, bodies of microscopically-visible size suspended in a liquid will perform movements of such magnitude that they can be easily observed in a microscope, on account of the molecular motions of heat”. Taking an explicit example of a spherical Brownian particle of radius one micron, he showed that the root-mean-square displacement would be of the order of a few microns when observed over a period of one minute.

Two intermediate steps of his calculation in this paper



are also extremely important. First, he obtained

$$\gamma D = k_B T = RT/N_{av}, \quad (2)$$

where γ is the coefficient of viscous drag force, D is the diffusion constant and T is the temperature. Note that D is a measure of the fluctuations in the positions of the Brownian particle while γ is a measure of energy dissipation; therefore, the formula (2) is a special case of the more general theorem, called fluctuation-dissipation theorem, which was derived half a century later.

The second important result was his derivation of the diffusion equation

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

for $P(x, t)$, the probability distribution of the position x of the Brownian particle at time t . Although diffusion equation was widely used already in the nineteenth century in the context of continuum theories, Einstein's derivation established a link between the random walk of a single particle and the diffusion of many particles (see [6] for an elementary discussion on this link).

For the initial condition $P(x, 0) = \delta(x)$, where $\delta(x)$ is the so-called Dirac delta function (see [7] for an elementary introduction to the delta function), the solution of the diffusion equation (3) is given by

$$P(x, t) = \frac{1}{[2\pi\sigma^2(t)]^{1/2}} e^{-x^2/(2\sigma^2)}, \quad (4)$$

where $\sigma^2(t) = 2Dt$. Thus, the root-mean-square displacement $\langle x^2 \rangle^{1/2}$, which corresponds to the width of the Gaussians, is proportional to \sqrt{t} .

Einstein's 1905 paper on Brownian motion was not the only paper he wrote on this topic. In fact, in the opinion of leading historians of science, Einstein's PhD. thesis,

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which was published in 1906, is perhaps a more important contribution to the theory of Brownian motion than his 1905 paper. But a detailed discussion of his later papers on this subject is beyond the scope of this article. Einstein also realized what would be the fate of kinetic theory in case experimental data disagreed with his predictions. he wrote, "...had the prediction of this movement proved to be incorrect, a weighty argument would be provided against the molecular-kinetic conception of heat".

Einstein's approach has been generalized by several of his contemporaries including Fokker, Planck, Smoluchowski and others. This general theoretical framework is now called the Fokker-Planck approach [12]. In this approach, one deals with a *deterministic* partial differential equation for a probability density; one example of the Fokker-Planck equation is that for $P(\vec{r}, \vec{v}; t)$, the probability that, at time t , the Brownian particle is located at \vec{r} and has velocity \vec{v} .

In 1900 Louis Bachelier's thesis entitled "Theorie de la Speculation" was examined by three of the greatest mathematician and mathematical physicists, namely, Paul Appell, Joseph Boussenesq and Henri Poincare. It was Poincare who wrote the report on that thesis which may be regarded as the pioneeing work on the application of mathematical theory of financial markets. In his thesis Bachelier postulated that the logarithm of a stock price executes Brownian motion with drift and he developed a mathematical theory which was, at least in spirit, very similar to the theory Einstein developed five years later [8]!

Smoluchowski

Unlike Einstein, Marian Smoluchowski was familiar with the literature on the experimental studies of Brownian motion. If he had not waited for testing his own the-



oretical predictions, the credit for developing the first theory of Brownian motion would go to him. He developed the theory much before Einstein but he decided to publish it only after he saw Einstein's paper which contained similar ideas. In his first paper, [9] published in 1906, Smoluchowski also pointed out the error in the Nageli-Ramsey objection against the original Cantoni-Delsaulx-Carbonelle argument. He clarified that each of the apparently straight segments of the Brownian trajectory is caused not by a single collision with a fluid particle, but by an enormously large number of successive kicks it receives from different fluid particles which, by rare coincidence, give rise to a net displacement in the same direction.

Perrin

Jean Perrin, together with his students and collaborators embarked on the experimental testing of Einstein's theoretical predictions. Their first task was to prepare a colloidal suspension with dispersed particles of appropriate size. They used gamboge, a gum extract, which forms spherical particles when dissolved in water. With the samples thus prepared, Perrin not only confirmed that the root-mean-square displacement of the dispersed particles grow with time t following the square-root law (1) but also made a good estimate of the Avogadro number. Einstein himself was surprised by the high level of accuracy achieved by Perrin and in a letter to Perrin he admitted "I did not believe that it was possible to study the Brownian motion with such a precision". It is true that the critics of molecular reality were silenced not by just one set of experiments of Perrin, but by the overwhelming evidence that emerged from almost identical estimates of the Avogadro number obtained by using many different methods. For his outstanding contribution, Jean Perrin was awarded the Nobel prize in 1926.

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Langevin

The Langevin approach [13] is based on a *stochastic* differential equation (that is, one in which only the statistical properties of the solution are calculable) for the individual Brownian particle and is, in spirit, closer to Newton's equation. In the *first approximation*, we can approximate the fluid by a *continuum*. Therefore, the classical equations of motion of the Brownian particle with mass M , position x and velocity v at time t , in an external force field F_{ext} can be written as

$$dx/dt = v \quad (5)$$

$$M(dv/dt) = F_{ext} - \Gamma v, \quad (6)$$

where, at this level of description, the viscous frictional drag Γ is treated as a phenomenological parameter.

However, on the scale of the size of a real Brownian particle the fluid does not appear to be a continuum. In fact, a Brownian particle “sees” that the fluid is made of molecules that constantly, but *discretely*, strike this Brownian particle, *accelerating* and *decelerating* it perpetually. “We witness in Brownian movement the phenomenon of molecular agitation on a reduced scale by particles very large on molecular scale ” [10]. A single collision has very small effect on the Brownian particle; the Brownian motion observed under a microscope is the *cumulative effect of a rapid and random sequence of large number of weak impulses*. Since the number of collisions suffered by the Brownian particle is very large, we do not intend to follow its path in any detail. Instead, we would like to have a *statistical* description of its movement.

Since equation (6) is a good first approximation, we *assume* that (6) correctly describes the *average* motion. We now incorporate the effects of the discrete collisions in a stochastic manner by *adding* a random *fluctuating*



force (with vanishing mean) to the frictional force term:

$$M(dv/dt) = F_{ext} - \Gamma v + F_{br}(t). \quad (7)$$

So far as the ‘fluctuating force’ (‘noise’) $F_{br}(t)$ is concerned, we *assume*:

- (i) $F_{br}(t)$ is independent of v , and
- (ii) $F_{br}(t)$ varies *extremely rapidly* as compared to the variation of v . Since ‘average motion’ is still assumed to be governed by the (6), we must have

$$\langle F_{br}(t) \rangle = 0; \quad (8)$$

the operational meaning of the symbol $\langle . \rangle$ will be explained in the next paragraph. Moreover, the assumption (ii) above implies that during small time intervals Δt , v and F_{br} change such that $v(t)$ and $v(t + \Delta t)$ differ infinitesimally but $F_{br}(t)$ and $F_{br}(t + \Delta t)$ have no correlation:

$$\langle \xi(t)\xi(t') \rangle = 2B\delta(t - t'), \quad (9)$$

where $\xi = F_{br}/M$ and, at this level of description, B is a phenomenological parameter. In order that the Brownian particle is in thermal equilibrium with the surrounding fluid, the constant B cannot be arbitrary; only a specific choice $B = \gamma k_B T$, where $\gamma = \Gamma/M$, guarantees the approach to the appropriate equilibrium Gibbsian distribution.

What is the operational meaning of the symbol $\langle . \rangle$ of averaging? The averaging is to be carried out over the distribution of the noise. This can be implemented practically in two alternative, but equivalent, ways:

either averaging over an ensemble of many systems consisting of a single Brownian particle in a surrounding fluid, *or* averaging over a number of Brownian particles in the same fluid, provided they are sufficiently far apart (possible at low enough density of the particles) so as not to influence each other.



What is meant by the term ‘solution’ of a stochastic equation like the Langevin equation? Suppose, we observe a Brownian particle under a microscope over a sufficiently long time interval $0 \leq t \leq T$ and obtain a record of its position $\vec{r}(t)$ as a function of time t . If the observations are made repeatedly, say N times, we get N trajectories

$$\vec{r}_1(t), \vec{r}_2(t), \dots, \vec{r}_N(t).$$

In general, these trajectories are all different, i.e., for a given $t = t^*$, $\vec{r}_1(t^*), \vec{r}_2(t^*), \dots, \vec{r}_N(t^*)$ are all different from each other. In other words, the motion of the Brownian particle is not reproducible and, therefore, not deterministic. Then, what can physics predict about Brownian motion on the basis of the Langevin equation? Although we are unable to make deterministic predictions, we make probabilistic ones.

If we repeat the observations a large number of times, we should be able to find empirically the distribution of $\vec{r}(t)$. In other words, we can calculate the probability $P(\vec{r}, t; \vec{r}_0, \vec{v}_0)$, which is the probability of finding the particle at position \vec{r} at time t , given that its initial position and velocity were \vec{r}_0 and \vec{v}_0 , respectively. Moreover, we can also calculate more detailed probability distributions like, for example, $P(\vec{r}, \vec{v}, t; \vec{r}_0, \vec{v}_0)$. However, we shall look at the moments of these distributions, e.g., $\langle \vec{v}(t) \rangle$, $\langle \vec{r}^2(t) \rangle$ by using the statistical properties of noise.

Calculation of the mean-square displacement, with the given initial position $x = 0$ at $t = 0$, leads to the final result (I leave it as an exercise for the students to go through the steps of the calculation following similar calculations given in [6])

$$\langle x^2 \rangle = \left(\frac{2k_B T}{\Gamma} \right) \left[t - \left(\frac{1}{\gamma} \right) (1 - e^{-\gamma t}) \right]. \quad (10)$$



Let us examine the two limiting cases. When $t \ll \gamma^{-1}$,

$$\langle x^2 \rangle \simeq (k_B T / M) t^2. \quad (11)$$

On the other hand, when $t \gg \gamma^{-1}$,

$$\langle x^2 \rangle \simeq (2k_B T / \Gamma) t. \quad (12)$$

Thus, the Brownian particle moves, effectively, ‘ballistically’ for times $t \ll \gamma^{-1}$ whereas for times $t \gg \gamma^{-1}$ it moves ‘diffusively’ with the effective diffusion coefficient $D = k_B T / \Gamma$. Note that (12) is identical to (1) derived earlier by Einstein through his diffusion equation approach.

Thus, the Langevin equation (7) is a *stochastic* dynamical equation that accounts for *irreversible* processes. On the other hand, in principle, one can write down the Newtonian equations of motion for the Brownian particle as well as that of all the other particles constituting the heat bath; each of these equations of motion will not only be *deterministic* but will also exhibit *time-reversal symmetry*. Note that, in the Langevin approach, one writes down only the equation (7) for the Brownian particle and does not explicitly describe the dynamics of the constituents of the heat bath. Therefore, a fundamental question is: how do the viscous damping term (responsible for irreversibility) and the random force term (which gives rise to the stochasticity) appear in the equation of motion of the Brownian particle when one ‘projects out’ the degrees of freedom associated with the bath variables and observes the dynamics in a tiny subspace of the full phase space of the composite system consisting of the Brownian particle + Bath?

To my knowledge, the simplest derivation of the stochastic Langevin equation for a Brownian particle, starting from the mutually coupled deterministic equations of motion (which are equivalent to Newton’s equation) for the Brownian particle and the molecules of the fluid,

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Suggested Reading

- [1] J Stachel, *Einstein's miraculous year: Five Papers that changed the face of physics* (Princeton University Press, 1998).
- [2] A Einstein, *Annalen der Phys*, Vol. 17, p.549, 1905.
- [3] The molecular constituents of matter speculated by ancient Indian philosopher Kanad were quite different from those proposed by the Greek philosophers.
- [4] J Bronowski, *The ascent of man*, Little Brown and Co., 1976.
- [5] C A Gearhart, *Am. J. Phys.*, Vol. 58, p.468, 1990.
- [6] S Sharma and Vishwamittar, *Resonance*, Aug., 2005.
- [7] Y B Zeldovich, *Higher mathematics for Beginners*, MIR publishers, 1973.
- [8] J Bernstein, *Am. J. Phys.*, Vol.73, p. 395, 2005.
- [9] M Smoluchowski, *Ann. Phys. Paris*, Vol 21, p.772, 1906.
- [10] S Chandrasekhar, *Rev. Mod. Phys.*, Vol. 15, p. 1, 1943.
- [11] R Zwanzig, *J.Stat. Phys.*, Vol. 9, p.215, 1973.
- [12] H Risken, *The Fokker-Planck Equation*, Springer, 2004.
- [13] W T Coffey, Yu P Kalmykov and J T Waldron, *The Langevin Equation*, Second edition, World Scientific, 2004.

was given by Robert Zwanzig [11]. For the simplicity of analytical calculations, he modelled the heat bath as a collection of harmonic oscillators (of unit mass, for simplicity) each of which is coupled to the Brownian particle. The differential equations satisfied by the position Q and the momentum P of the Brownian particle have the general form

$$\dot{Q} = P/M \quad (13)$$

$$\dot{P} = F_{ext}(Q) + \sum_j \gamma_j \left(q_j - \frac{\gamma_j Q}{\omega_j^2} \right), \quad (14)$$

where F_{ext} is the external force (not arising from the reservoir), $q_j(t)$ and $p_j(t)$ denote the positions and momenta, respectively, of the j -th harmonic oscillator constituent of the reservoir while the dot on a variable denotes derivative with respect to time. The motion of the Brownian particle is influenced by that of the bath variables because of the coupling term $\gamma_j q_j$ on the right hand side of (14). Similarly, the equations of motion for the bath variables are

$$\dot{q}_j = p_j \quad (15)$$

$$\dot{p}_j = -\omega_j^2 \left(q_j - \frac{\gamma_j Q}{\omega_j^2} \right) = -\omega_j^2 q_j + \gamma_j Q, \quad (16)$$

where the motion of the bath variables are influenced by the Brownian particle through their coupling introduced by the last term on the right hand side of (16).

The simple analytical calculation shown in *Box 1* demonstrates how both the dissipative viscous drag term and the noise term appear in the equation of motion of the Brownian particle in this model when the bath degrees of freedom are projected out. Thus, the molecules in the fluid medium which give the random 'kicks' to the Brownian particle are also responsible for its energy dissipation because of viscous drag. The incessant random motion of the Brownian particle is maintained for ever by the delicate balance of the random kicks it gets



Box 1.

Taking derivatives of the auxiliary variables $x_j^\pm = p_j \pm i\omega_j q_j$ w.r.t. time we get

$$\dot{x}_j^\pm = \dot{p}_j \pm i\omega_j \dot{q}_j = Q\gamma_j \pm i\omega_j x_j^\pm.$$

The formal solutions of these two equations are

$$x_j^\pm(t) = e^{\pm i\omega_j t} x_j^\pm(0) + \gamma_j \int_0^t dt' e^{\pm i\omega_j(t-t')} Q(t').$$

Subtracting one from the other, we get

$$\begin{aligned} 2i\omega_j q_j &= e^{i\omega_j t} \{p_j(0) + i\omega_j q_j(0)\} - e^{-i\omega_j t} \{p_j(0) - i\omega_j q_j(0)\} \\ &\quad + 2\gamma_j i \int_0^t dt' [\sin\{\omega_j(t-t')\}] Q(t'). \end{aligned}$$

Evaluating the integral on the right hand side by parts we get

$$\begin{aligned} I &= \int_0^t dt' [\sin\{\omega_j(t-t')\}] Q(t') \\ &= \frac{Q(t)}{\omega_j} - \frac{Q(0)}{\omega_j} \cos(\omega_j t) - \int_0^t dt' \dot{Q}(t') \left[\frac{\cos\{\omega_j(t-t')\}}{\omega_j} \right] \end{aligned}$$

and, hence,

$$\begin{aligned} q_j(t) - \frac{\gamma_j}{\omega_j^2} Q(t) &= \left[\frac{p_j(0)}{\omega_j} \right] \sin(\omega_j t) + \left\{ q_j(0) - \frac{\gamma_j}{\omega_j^2} Q(0) \right\} \cos(\omega_j t) \\ &\quad - \left(\frac{\gamma_j}{\omega_j^2} \right) \int_0^t dt' \frac{P(t')}{M} \cos\{\omega_j(t-t')\}. \end{aligned}$$

Substituting this expression for $q_j(t)$ into the equation for \dot{P} we get

$$\dot{P} = F_{ext}(Q) - \int K(t-t') \dot{Q}(t') dt' + \eta(t),$$

where

$$\begin{aligned} K(t-t') &= \sum_j \left(\frac{\gamma_j^2}{\omega_j^2} \right) \left[\cos\{\omega_j(t-t')\} \right], \\ \eta(t) &= \sum_j \gamma_j \left[\left\{ q_j(0) - \left(\frac{\gamma_j}{\omega_j^2} \right) Q(0) \right\} \cos(\omega_j t) + \left\{ \frac{p_j(0)}{\omega_j} \right\} \sin(\omega_j t) \right]. \end{aligned}$$

Box 1. continued...



But, in practice, it is impossible (and unnecessary) to know the initial conditions of all the oscillators as, by definition, the number of degrees of freedom associated with the bath is very large. Therefore, let us assume that *only statistical properties of these initial conditions are known*; suppose, the distributions of

$$p_j(0) \text{ and } q_j(0) - (\gamma_j/\omega_j^2)Q(0),$$

are Gaussian and that the temperature of the bath is T such that

$$\langle p_j(0) \rangle = 0 = \langle q_j(0) - \left(\frac{\gamma_j}{\omega_j^2}\right)Q(0) \rangle$$

$$\langle p_i(0)p_j(0) \rangle = k_B T \delta_{ij} \left\langle \left[q_i(0) - \left(\frac{\gamma_i}{\omega_i^2}\right)Q(0) \right] \left[q_j(0) - \left(\frac{\gamma_j}{\omega_j^2}\right)Q(0) \right] \right\rangle = \left(\frac{k_B T}{\omega_j^2}\right) \delta_{ij}.$$

Using these assumptions, it is straightforward to verify that $\langle \eta(t) \rangle = 0$ and

$$\langle \eta(t)\eta(t') \rangle = k_B T K(t - t').$$

Thus, the equation for \dot{P} becomes a generalized Langevin equation.

In order to correlate the original form of the Langevin equation proposed by Langevin with the generalized Langevin equation derived above, we first convert the expression $K(t - t')$ into an integral:

$$K(t - t') = \int_0^\infty \left(\frac{\gamma^2}{\omega^2}\right) \cos\{\omega(t - t')\} P(\omega) d\omega,$$

where $P(\omega)d\omega$ is the number of frequencies in the interval between ω and $\omega + d\omega$. If we now choose

$$P(\omega) \left(\frac{\gamma^2}{\omega^2}\right) = \Gamma,$$

we get

$$K(t - t') = \Gamma \int_0^\infty \cos\{\omega(t - t')\} d\omega = \Gamma \lim_{\omega \rightarrow \infty} \left[\frac{\sin\{\omega(t - t')\}}{t - t'} \right] = \Gamma \delta(t - t')$$

and, in this case, the generalized Langevin equation reduces to the original form of the Langevin equation.

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from the fluid particles and the energy it dissipates back into the fluid via viscous drag. Therefore, it should not be surprising that these two manifestations of the fluid medium are related through the Einstein relation (2).

