A simple model for Brownian motion leading to the Langevin equation

Bart G. de Grooth
Department of Applied Physics, University of Twente, P.O. Box 217, 7500AE Enschede, The Netherlands

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A simple one-dimensional model is presented for the motion of a Brownian particle. It is shown how the collisions between a Brownian particle and its surrounding molecules lead to the Langevin equation, the power spectrum of the stochastic force, and the equipartition of kinetic energy.

I. INTRODUCTION

In the last several years many techniques have become available that enable the study of individual molecules. Examples are imaging techniques such as the scanning tunneling microscopes[1] and the atomic force microscope (AFM),[2] direct measurement of the forces between individual molecules using AFM[3] and optical trapping techniques,[4] the measurement of the fluorescence of single molecules using confocal laser scanning microscopes,[5] and near-field scanning optical microscopy.[6] These techniques have made it possible to study the dynamical behavior of individual functional systems such as motor proteins[7] and DNA transcription enzymes.[8]

These techniques also confront us with the fundamental limits due to thermal fluctuations. The motion of a cantilever of an AFM due to its interaction with the surrounding molecules limits the accuracy by which we can measure the forces between the tip and the sample.[9] Attempts to obtain DNA sequence information by measuring the rupture forces upon unzipping the strands of a single DNA molecule are hampered by the thermal motions of the two single strands formed.[10]

To obtain a better physical understanding of the dynamical behavior of individual biomolecules,[11] a good understanding of thermal fluctuations is needed. The usual starting point is the Langevin equation, whose form is assumed in most textbooks without a discussion of how the collisions between a Brownian particle and its much lighter surrounding molecules give rise to a dissipative and a stochastic force. Gillespie has shown recently that a simple Markov process leads to a dissipative force.[12] The goal of this article is to discuss an even simpler model for the dynamics of a Brownian particle and to show in detail how it leads to the essential features of more realistic systems.

The model consists of a relatively heavy particle (the Brownian particle) moving in one dimension subject to random collisions with the surrounding molecules. We will show that a straightforward analysis leads to two forces on the Brownian particle: a dissipative force proportional to the velocity of the Brownian particle and a random fluctuating force with zero average. Because both terms are the consequence of the collisions between the Brownian particle and the surrounding molecules, we obtain a direct relation between the two forces leading to the fluctuation dissipation theorem.

In Sec. III we show how the model can be used to obtain an algorithm for doing numerical simulations of a Brownian particle in the presence of arbitrary forces. In Sec. IV the model is used to determine the power spectrum of the stochastic force, and in Sec. V it is shown how this power spectrum is related to the power spectra of the position and velocity of a Brownian particle for a particle in a harmonic potential. Finally, in Sec. VI we summarize our results.

II. SIMPLE ONE-DIMENSIONAL MODEL LEADING TO THE LANGEVIN EQUATION

We consider a one-dimensional system consisting of a relatively large particle (the Brownian particle) with mass M which is hit from both sides by molecules of mass m, with $M \gg m$. The collisions are assumed to be elastic. We first consider a single collision and designate the velocity of the Brownian particle before and after the collision by V and V', respectively. Similarly, the velocity of a molecule before and after the collision is v and v'. If we combine the equations for conservation of momentum and energy, we can write the velocities after the collision in terms of the velocities before the collision:

$$V' = \frac{M-m}{M+m} V + \frac{2m}{M+m} v, \tag{1}$$

$$v' = \frac{m-M}{M+m} v + \frac{2M}{M+m} V. \tag{2}$$

We first show that the behavior of the system satisfies the equipartition theorem provided that (i) v is independent of V, and (ii) the time between successive collisions is independent of V. In a system consisting of a very large number of molecules of mass m that behave as a thermal bath, the first condition is fulfilled. The second condition is not obviously satisfied, because we might expect that the time between collisions would be smaller for a fast moving Brownian particle. However, if $v \gg V$, the number of collisions per unit time is dominated by the movement of the molecules.[13] The second condition implies that the time average of a quantity equals the average over a large number of collisions:

$$\langle V^2 \rangle = \lim_{T\to\infty} \frac{1}{T} \int_0^T V(t)^2 dt = \lim_{N\to\infty} \frac{\Sigma_{i=0}^{N-1} t_i V_i^2}{\Sigma_{i=0}^{N-1} t_i}$$

$$= \lim_{N\to\infty} \frac{\overline{t} \Sigma_{i=0}^{N-1} V_i^2}{\Sigma_{i=0}^{N-1} t_i} = \lim_{N\to\infty} \frac{1}{N} \sum_{i=0}^{N-1} V_i^2 = \overline{V^2}, \tag{3}$$

where V_i is the velocity of the Brownian particle between the ith and $(i+1)$th collision, t_i is the time interval between these collisions, and N is the number of collisions during the time interval T. The brackets denote a time average and the bar denotes averages over collisions. The average time interval between collisions is given by $\overline{t} = \Sigma_{i=0}^{N-1} t_i / N$. We have

used condition (ii) to obtain the third equality in Eq. (3).[14]

We take the square of Eq. (1) and average over the N collisions. In the limit $N\to\infty$, we obtain:

$$\overline{V'^2}=\frac{(M-m)^2}{(M+m)^2}\overline{V^2}+\frac{4m^2}{(M+m)^2}\overline{v^2}+2\left(\frac{M-m}{M+m}\right)\left(\frac{2m}{M+m}\right)\overline{Vv}. \tag{4}$$

For a stationary system we have $\overline{V'^2}=\overline{V^2}$, and condition (i) implies that $\overline{Vv}=\overline{V}\,\overline{v}=0$. Hence, we obtain the result

$$M\overline{V^2}=m\overline{v^2}. \tag{5}$$

We see that given these two conditions, the average of the kinetic energy of the Brownian particle is the same as that of the surrounding molecules, in agreement with the equipartition theorem.

We now proceed to obtain the Langevin equation. We use the assumption $M\gg m$ to write:

$$\frac{M-m}{M+m}\approx 1-2\frac{m}{M}+O\left(\left(\frac{m}{M}\right)^2\right), \tag{6}$$

$$\frac{M}{M+m}\approx 1-\frac{m}{M}+O\left(\left(\frac{m}{M}\right)^2\right), \tag{7}$$

$$\frac{m}{M+m}\approx \frac{m}{M}+O\left(\left(\frac{m}{M}\right)^2\right). \tag{8}$$

With these approximations Eq. (1) can be rewritten as:

$$V'=\left(1-\frac{2m}{M}\right)V+\frac{2m}{M}v. \tag{9}$$

From Eq. (9) we see that the change in momentum of the Brownian particle due to a single collision equals

$$\Delta P=2mv-2mV. \tag{10}$$

Equation (10) shows that the change of momentum of a Brownian particle due to collisions with its surrounding molecules results in two contributions. The momentum change due to the first term is positive or negative, but on the average this contribution is zero because collisions from the left and right have the same probability. The second contribution tends to reduce the speed of the Brownian particle and is a damping term proportional and opposite to the velocity of the Brownian particle.[15]

Let us look at what happens during a time interval Δt which is small enough that the velocity of the Brownian particle does not change appreciably, but because $M\gg m$, we still have a large number of collisions. From Eq. (10) we can write the momentum change of the Brownian particle due to N collisions as:

$$\Delta P_N=2m\sum_{i=0}^{N-1}v_i-2m\sum_{i=0}^{N-1}V_i. \tag{11}$$

Because the velocity of the Brownian particle is assumed to not change appreciably during Δt, we can approximate the second sum in Eq. (11) by $2mNV=2mnV(t)\Delta t$, where $V(t)$ is the velocity of the Brownian particle at time t, and n is the mean number of collisions per second so that $N=n\Delta t$. Hence, we write

$$\Delta P_N=2m\sum_{i=0}^{n\Delta t-1}v_i-2mnV(t)\Delta t. \tag{12}$$

We divide both sides of Eq. (12) by Δt and obtain a formal expression for the time derivative of the Brownian particle's velocity:

$$M\frac{dV}{dt}=F_s-\gamma V, \tag{13}$$

where the stochastic force F_s is defined as

$$F_s=\frac{1}{\Delta t}\sum_{i=0}^{n\Delta t-1}2mv_i, \tag{14}$$

and the damping constant γ is given by

$$\gamma=2mn. \tag{15}$$

Equation (13) has the form of the Langevin equation[16] with explicit expressions for the damping and stochastic forces in the model. From Eq. (15) we see that the damping constant γ is proportional to the number of collisions per second and the mass of the surrounding molecules. In the above derivation we assumed that Δt contains a large number of collisions. For this reason dV/dt in Eq. (13) should be interpreted with caution. It is referred to as a ''coarse grained time derivative.''[17]

The equipartition theorem can be used to arrive at the well known relation between the fluctuations of the position of a Brownian particle (in the absence of an external force) and γ:[16]

$$\langle\Delta x^2\rangle=\frac{2k_BT}{\gamma}t, \tag{16}$$

where k_B is Boltzmann's constant and T is the absolute temperature. Equation (16) is an example of the fundamental relation between fluctuations and dissipation. We can understand the basis of this relation from Eq. (15). A large damping constant implies many collisions per second, which results in a reduction of the persistent motion of the Brownian particle.

Dissipation would also occur if the collisions with the molecules were not randomly distributed, but occurred at a regular interval of $1/n$. In that case the motion of the particle would be damped (dissipation), but would not fluctuate and hence Eq. (16) would not be applicable. The reason for the relation between dissipation and fluctuation is that the time between collisions is a random variable.

III. NUMERICAL SIMULATIONS OF BROWNIAN MOTION

To obtain a better understanding of Brownian motion under different conditions, computer simulations can be very helpful. We start with the Langevin equation (13) and divide the time into q intervals so that $t=q\Delta t$. Using Eq. (13), the new velocity V_{q+1} can be expressed in terms of the previous velocity V_q as

$$V_{q+1}=V_q-\gamma\frac{V_q}{M}\Delta t+\Delta V_s, \tag{17}$$

where ΔV_s is the velocity change due to the stochastic term in Eq. (13). The damping term poses no difficulty as long as

the velocity change during the interval Δt is small compared to $\sqrt{k_B T/M}$. Our main problem is to find a useful expression for the stochastic term in Eq. (17). If the time between iterations were sufficiently small, the procedure would be straightforward. For each iteration we determine from a random drawing whether a collision has taken place or not. The probability of a collision is such that on the average, there are $1/n$ collisions with an equal chance of a collision from the left or the right. If there is no collision, the new velocity can be calculated from Eq. (17) with $\Delta V_s = 0$. If a collision occurs, the stochastic term in Eq. (17) is given by [see Eq. (10)]:

$$\Delta V_s = \frac{2mv}{M} = \frac{2}{M}\frac{v}{|v|}\sqrt{m^2 v^2} = \frac{2}{M}\frac{v}{|v|}\sqrt{m k_B T} = \frac{1}{M}\frac{v}{|v|}\sqrt{\frac{2\gamma}{n}k_B T}. \quad (18)$$

We have used Eq. (15) and have set the kinetic energy of the molecules to be $\frac{1}{2}k_B T$. For simplicity, we have assumed that all molecules have the same kinetic energy.

The difficulty is that in practice the number of collisions necessary to change the velocity of the Brownian particle appreciably is so high that the above algorithm would take too much computing time. Therefore, we have to find an expression for the contribution of a relatively large number of collisions p, where $p \gg 1$. For a realistic Brownian particle of 1 μm, the velocity change of $p = 1000$ collisions with the surrounding molecules would still be very small. Because the collisions occur randomly from the left and right, the effect of p collisions follows a binomial distribution with no average velocity change and a half width equal to the square root of $p/2$ times the magnitude of the velocity change due to a single collision. For p sufficiently large, the binomial distribution can be approximated by a Gaussian distribution. Therefore, we can write for the velocity change after p collisions:

$$\Delta V_p = w_q \sqrt{\frac{p}{2}}\Delta V_1 = \frac{w_q}{M}\sqrt{\frac{p}{n}\gamma k_B T} = \frac{w_q}{M}\sqrt{\gamma k_B T \Delta t}, \quad (19)$$

where we used Eq. (18) and $\Delta t = p/n$. The variable w_q is sampled randomly from a Gaussian distribution with zero average and a variance equal to 2. Such a random variable can be obtained by calculating the sum:

$$w_q = \sqrt{2}\sum_{i=1}^{12}\left(r_i - \frac{1}{2}\right), \quad (20)$$

where r_i is uniformly distributed in the unit interval.

These considerations lead to the following algorithm for the simulation of the Langevin equation:[18]

$$V_{q+1} = V_q - \gamma\frac{V_q}{M}\Delta t + \frac{w_{q+1}}{M}\sqrt{\gamma k_B T \Delta t} + \frac{F_{\text{ext}}}{M}\Delta t, \quad (21)$$

$$X_{q+1} = X_q + V_{q+1}\Delta t. \quad (22)$$

An additional external force F_{ext} has been added for generality. The algorithm in Eqs. (21) and (22) is primarily intended to illustrate the physical origin of the stochastic term. More efficient algorithms can be found in the literature.[19]

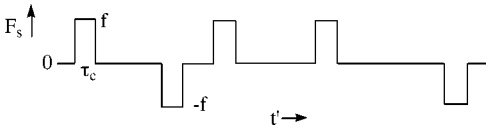

Fig. 1. The stochastic force is approximated by a constant force f during a collision time τ_c and is otherwise zero.

An interactive computer program which uses this algorithm to simulate a Brownian particle in a single or double potential well (the Kramers problem[20]) can be downloaded from the author's Web site.[21]

IV. POWER SPECTRUM OF THE STOCHASTIC FORCE

Because the statistical behavior of the motion of a Brownian particle is related to $|\tilde{F}_s(\omega)|^2$, the power spectrum of the stochastic force F_s (see Sec. V), we now derive an expression for $|\tilde{F}_s(\omega)|^2$. From the Wiener–Khintchine theorem $|\tilde{F}_s(\omega)|^2$ is determined from the autocorrelation function of F_s:[22]

$$|\tilde{F}_s(\omega)|^2 = 2\int_{-\infty}^{\infty} e^{-i\omega t}\langle F_s(t')F_s(t'+t)\rangle\, dt, \quad (23)$$

where $\tilde{F}_s(\omega)$ is the Fourier transform of $F_s(t)$. The brackets indicate time averaging over t'.

To obtain an expression for the autocorrelation function of F_s, we first consider a single collision whose duration is τ_c. The momentum change of the Brownian particle from the stochastic force due to a single collision is according to Eq. (10) given by

$$\Delta P_s = 2mv. \quad (24)$$

Hence, the average force during the collision is

$$f = \frac{2mv}{\tau_c}. \quad (25)$$

The simplest model for the interaction is to assume a constant force f during the collision time τ_c as shown in Fig. 1.

Due to the stochastic nature of F_s, the correlation between $F_s(t')$ and $F_s(t'+t)$ differs from zero only if $|t| < \tau_c$. To obtain the time average of $F_s(t')F_s(t+t')$, it is sufficient to average this function during the mean time between collisions, $\tau = 1/n$. If $|t| < \tau_c$, the average correlation is given by

$$\langle F_s(t')F_s(t'+t)\rangle = \frac{1}{\tau}\left\langle \int_0^{\tau} F_s(t')F_s(t'+t)_{\text{one collision}}\, dt' \right\rangle = \langle f^2\rangle\frac{[\tau_c - |t|]}{\tau}, \quad (26)$$

whereas if $|t| > \tau_c$, the correlation is zero (see Fig. 2). Using Eqs. (25) and (15), the relation $\tau = 1/n$, and writing $\frac{1}{2}k_B T$ for the average kinetic energy of the molecules, we can rewrite Eq. (26) as:

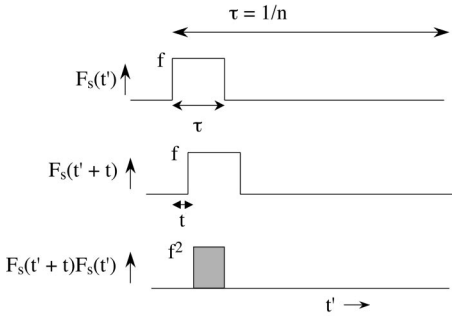

Fig. 2. To calculate the time average of the autocorrelation function of F_s, we can average during a single ''cycle,'' the time between two collisions $1/n$. The autocorrelation is indicated by the area of the dashed square.

$$\langle F_s(t')F_s(t'+t)\rangle = \langle f^2\rangle \frac{[\tau_c - |t|]}{\tau} = \frac{\langle 4m^2v^2n\rangle}{\tau_c^2}[\tau_c - |t|]$$
$$= 2\gamma k_B T \frac{[\tau_c - |t|]}{\tau_c^2} \qquad (27)$$

for $|t| < \tau_c$.

In summary we have:

$$\langle F_s(t')F_s(t'+t)\rangle = \begin{cases} 2\gamma k_B T[\tau_c - |t|]/\tau_c^2 & \text{for } |t| < \tau_c \\ 0 \quad \text{for } |t| > \tau_c \end{cases}. \qquad (28)$$

This function is drawn in Fig. 3.

If we assume that the duration of the collisions is very short, we can approximate the autocorrelation function by a delta function. In order to obtain the correct normalization, we integrate Eq. (28) with respect to t which gives:

$$\int_{-\tau_c}^{\tau_c} \langle F_s(t')F_s(t'+t)\rangle dt = 2\gamma k_B T, \qquad (29)$$

where we have used:

$$\int_{-\tau_c}^{\tau_c} [\tau_c - |t|]dt = 2\int_0^{\tau_c} (\tau_c - t)dt = \tau_c^2. \qquad (30)$$

It follows that the form

$$\langle F_s(t')F_s(t'+t)\rangle = 2\gamma k_B T \delta(t) \qquad (31)$$

is consistent with Eq. (29). Equation (31), which gives a direct relation between the spectral properties of the stochastic force and the dissipation of the system, is sometimes referred to as the fluctuation dissipation theorem.[23] Using Eq. (23), we obtain the power spectrum of F_s:

$$|\tilde{F}_s(\omega)|^2 = 4\gamma k_B T. \qquad (32)$$

We see that the power spectrum is independent of the frequency, that is, there is a white noise spectrum. In reality we know that there are correlations during the collision time

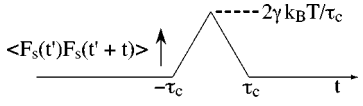

Fig. 3. The average autocorrelation function of the stochastic force as a function of the time interval t.

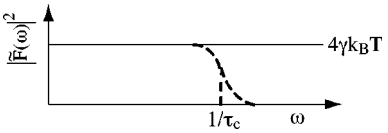

Fig. 4. The power spectrum of the stochastic force given by Eq. (32) is independent of the frequency. In reality, it drops to zero for frequencies above the inverse of the collision time.

which means that frequencies above $1/\tau_c$ are absent (see Fig. 4).

V. POWER SPECTRUM OF THE DISPLACEMENT AND THE VELOCITY OF A BROWNIAN PARTICLE

Because the behavior of a particle subjected to Brownian motion is stochastic, we have to look at its statistical properties to obtain a quantitative description. From experiments it is easy to determine the power spectra of the square of position and velocity. By analyzing these spectra we can deduce the relevant parameters.

We consider a one-dimensional system consisting of a particle of mass M in a harmonic potential (with force constant k), damping γ, subject to a stochastic force F_s. For this system we can write the Langevin equation in Eq. (13) as

$$M\ddot{x} + \gamma\dot{x} + kx = F_s(t). \qquad (33)$$

We can express the statistical behavior of x and v of this particle by taking the Fourier transform of Eq. (33). We write

$$\tilde{F}(\omega) = \int_{-\infty}^{\infty} F_s(t)e^{-i\omega t}dt,$$
$$F_s(t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} \tilde{F}(\omega)e^{i\omega t}d\omega \qquad (34)$$

and a similar expression for $\tilde{x}(\omega)$, and we obtain for the Fourier transform of Eq. (33):[24]

$$\tilde{x}(\omega)[k - i\gamma\omega - M\omega^2] = \tilde{F}_s(\omega). \qquad (35)$$

If we multiply Eq. (35) by its complex conjugate, we find:

$$\langle|\tilde{x}(\omega)|^2\rangle = \frac{\langle|F_s(\omega)|^2\rangle}{(M\omega^2 - k)^2 + \gamma^2\omega^2}. \qquad (36)$$

We see that the power spectrum of x is directly related to that of the stochastic force. Using Eq. (32) for the stochastic force originating from random collisions, we obtain:

$$\langle|\tilde{x}(\omega)|^2\rangle = \frac{4\gamma k_B T}{(M\omega^2 - k)^2 + \gamma^2\omega^2}. \qquad (37)$$

Similarly, we find for the power spectrum of the squared velocity:

$$\langle|\tilde{v}(\omega)|^2\rangle = \frac{4\omega^2\gamma k_B T}{(M\omega^2 - k)^2 + \gamma^2\omega^2}. \qquad (38)$$

Equations (37) and (38) can be used to fit the experimentally measured power spectra from which the values of the parameters M, k and γ can be deduced.[25]

We have approximated the power spectrum of $F_s(\omega)$ by a constant function, which means that all frequencies are as-

sumed to be present (white noise). As we have noted, in reality, frequencies above the inverse of the collision time are absent. We can now see that this approximation does not change the frequency dependence of the power spectra for all practical cases. The numerator in Eq. (36) goes to zero for $\omega > k/\gamma$, which in realistic systems occurs at frequencies that are much smaller than $1/\tau_c$. In other words, whether or not the stochastic force contains frequencies higher than $1/\tau_c$ is not important for the behavior of the system because the system is much too slow to respond to such high frequencies.

Finally, it is reassuring to find that the derived expressions for v and x are in agreement with the equipartition theorem. To see this we use Parseval's theorem

$$\int |y(t)^2 dt = \frac{1}{2\pi} \int |\tilde{y}(\omega)|^2 d\omega, \tag{39}$$

and perform the integration using Eq. (37) or (38). Note that we have not made use of the equipartition theorem, so the outcome indicates that our model implies the equipartition of kinetic energy between the Brownian particle and the molecules, in agreement with our expectations at the beginning of Sec. II.

VI. CONCLUSIONS

We have studied a simple one-dimensional model for the interaction of a Brownian particle with its surroundings. We obtained insight into how this interaction leads to the fluctuations and a dissipation force in the Langevin equation, the equipartition of kinetic energy, and the power spectra. It is hoped that this simple model can lead to a better understanding and physical intuition of about real systems.

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[14]According to condition (ii), t_i is independent of V_i, and hence we can replace the product $t_i V_i^2$ in Eq. (3) by $t_j V_i^2$. For $N \to \infty$, we can replace t_j by the average interval time $\bar{t}$ from which the third equality of Eq. (3) follows.
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