Brownian Motion in a Classical Ideal Gas: a Microscopic Approach to Langevin’s Equation

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We present an insightful “derivation” of the Langevin equation and the fluctuation dissipation theorem in the specific context of a heavier particle moving through an ideal gas of much lighter particles. The Newton’s Law of motion ($m\ddot{x} = F$) for the heavy particle reduces to a Langevin equation (valid on a coarser time scale) with the assumption that the lighter gas particles follow a Boltzmann velocity distribution. Starting from the kinematics of the random collisions we show that (1) the average force $\langle F \rangle \propto -\dot{x}$ and (2) the correlation function of the fluctuating force $\eta = F - \langle F \rangle$ is related to the strength of the average force.

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I. INTRODUCTION

In recent years, many experiments on single large molecules like colloidal spheres and bio-polymers, have been reported [1]. Many of these experiments focus on the kinematics of motion of these large molecules through typical fluid environments, at room temperature. Most theoretical explanations of these experiments [1, 2] neglect the intrinsic correlations of the surrounding fluid and treat the fluid as a bath, generating friction and uncorrelated noise on the large molecule, exactly the way a Brownian particle is treated.

This approach may fail if the molecule is large or if it is close to a hard wall such that the displaced fluid due to its motion does not return to equilibrium immediately. In that case one may have to solve the Navier-Stokes equation to correctly incorporate the dynamics of the fluid, for example while deriving the Stokes’ law [3]. Further, extended macromolecules of the polymer variety, where one part of the molecule disturbs the fluid which in turn affects the other parts of the molecule (the so called hydrodynamic effect [4]) require yet another kind of analysis. It is however worthwhile and desirable to gain more physical insight and understanding into the simple yet intriguing situation of the Brownian motion, for its own sake and also to come up with meaningful models for more complicated situations. We revisit the problem of Brownian motion through an ideal gas in this work.

When a particle, substantially heavier than the gas particles, is injected into the gas, it is randomly kicked around by the gas molecules. However, due to the heavier nature of this particle (usually called the Brownian particle) it takes a bunch of small kicks by the gas molecules, over a time interval, to move the Brownian particle appreciably. Thus there occurs a natural separation of time scales for the motion of this heavier particle and the gas molecules [5, 6]. The motion of a Brownian particle, on a coarse grained time scale is usually described by the Langevin equation [6, 7],

$$M\ddot{x} + \Gamma \dot{x} = \eta.$$  \hspace{1cm} (1.1)

where $x$ is the position of the Brownian particle. The overall effect of collisions is modeled by introducing the damping coefficient $\Gamma$ and a random force $\eta$ with zero mean. This is a physically motivated phenomenological equation where the effect of collisions is neatly separated into velocity dependent friction and a random noise obeying FDT. Mostly, the Langevin equation is motivated from a phenomenological point of view. Every derivation of the Langevin equation requires certain assumptions; Mori and Zwanzig have...
II. BROWNIAN MOTION IN AN IDEAL GAS WITH MEAN FREE PATH $\lambda \to \infty$

Consider a Brownian particle ‘B’ moving in a gas along the $x$ direction with a velocity $v_0$. To find the friction coefficient $\Gamma$, we have to calculate the net force on B due to collisions with the gas molecules. Consider the simplest possible geometry for B, that of a plate moving with a velocity perpendicular to its plane (In appendix A, the calculation is extended to a spherical particle). It is easier to capture the essentials of the calculation in this case without getting lost in the geometrical factors. The easiest way to arrive at the force is to treat all collisions in the rest frame of the Brownian particle. If a molecule comes in with a velocity $v$ then from the conservation of energy and momentum, it follows that it is reflected with a velocity $-\kappa v$

$$\kappa = \frac{M - m}{M + m}$$ (2.1)

$M$ and $m$ being the masses of the Brownian particle and of the gas molecule respectively. For $M \gg m$, the momentum transferred to B per collision is then

$$\delta p = (1 + \kappa)mv$$ (2.2)

The force on $B$ is the momentum transferred to it per unit time, for which we need to know the number of collisions per unit time for each value of $v$. This number for a given $v$ is the number of molecules in the (slanted) cylinder of edge length $|v|$ swept in unit time as shown in Figure 1, i.e.

$$N_{col} = A \frac{\rho}{m} |v_x|,$$ (2.3)

where $A$ is the area of cross section of the plate and $\rho$ the density of the gas. The force on $B$ is $N_{col}$ times the momentum transfer in each collision, integrated over all possible velocities:

$$\mathbf{F} = -A\rho(1 + \kappa) \int d\mathbf{v} P_z(v) |v_x| \mathbf{v}.$$ (2.4)

where $P_z(v)$ is the distribution of velocities in the frame of the Brownian particle. The distribution in the lab
frame is Maxwellian i.e.,
\[
P(v_x, v_y, v_z) = P_0(v_x)P_0(v_y)P_0(v_z)
\]
\[
P_0(v_x) = \frac{1}{\sqrt{2\pi}\sigma} e^{-\frac{v_x^2}{2\sigma^2}} \quad (2.5)
\]
where \(\sigma\) is the mean thermal velocity component in one direction.

\[
\sigma^2 = \langle v_x^2 \rangle_{th} = \frac{k_B T}{m}
\]  
(2.6)

If the velocity of a gas molecule is \(v\) in the co-moving frame, then it is \(v + u_0\hat{x}\) in the lab frame. Therefore the distribution in the co-moving frame is,
\[
P_c (v_x, v_y, v_z) = P_0(v_x + u_0)P_0(v_y)P_0(v_z)
\]  
(2.7)

The component of the force perpendicular to \(\hat{x}\) adds up to zero whereas the \(x\) component is
\[
F_x = A\rho(1 + \kappa) \int_{-\infty}^{\infty} dv_x P_0(v_x + u_0)|v_x|v_x
\]
\[
= A\rho(1 + \kappa) \int_{-\infty}^{\infty} dv_x P_0(v_x)|v_x - u_0|(v_x - u_0)
\]  
(2.8)

After a few simple manipulations, we get:
\[
F_x = -2A\rho(1 + \kappa)e^{-\frac{v_0^2}{2\sigma^2}} \int_{0}^{\infty} dv_x v_x^2 \frac{1}{\sqrt{2\pi}} e^{-\frac{v_x^2}{2\sigma^2}} \text{sinh} \left(\frac{v_x u_0}{\sigma^2}\right)
\]  
(2.9)

It may be noted that the force is an odd function of \(u_0\), in keeping with the general rule that dissipative terms in an equation of motion violate time reversal invariance. For small velocities \(u_0\), we can Taylor-expand to the lowest order in \(u_0\) to get
\[
F_x = -2A\rho(1 + \kappa)u_0\sigma \frac{1}{\sqrt{2\pi}} \int_{0}^{\infty} dx x^3 e^{-\frac{x^2}{2\sigma^2}}
\]  
(2.10)

We call the dimensionless integral in the above equation \(\chi_3\) (Appendix B). The final expression for the force then is:
\[
F_x = -2A\rho(1 + \kappa)u_0 \sigma \chi_3
\]  
(2.11)
from which we read off the friction coefficient
\[
\Gamma = 2A\rho(1 + \kappa)\sigma \chi_3
\]  
(2.12)

The friction coefficient is not proportional to the linear dimension of the particle (as it is in the Stokes’ Law) but rather to the area. This result carries over to the case of the sphere as well. The area comes because the gas we are considering is ideal and the motion of the Brownian particle in no way affects the flow of the gas. The Stokes’ result essentially derives from the fact that the fluid (being a strongly interacting gas) makes way for the particle as it moves through it.

Let us now proceed with the calculation of the noise. In the standard Langevin equation (1.4) the noise \(\eta\) has to satisfy the fluctuation dissipation theorem
\[
\langle \eta(t)\eta(\tilde{t}) \rangle = 2k_B T \Gamma \delta(t - \tilde{t}) \quad (2.13)
\]
This theorem relies on the requirement that the Brownian particle is in thermal equilibrium with the gas it is moving through.

Before we derive the fluctuation dissipation theorem, we coarse grain the time in terms of a small time unit \(\epsilon\), chosen such that several collisions take place within \(\epsilon\) time, while the Brownian particle does not move appreciably during this interval. For a massive enough particle it is always possible to find such a time. It is simplest to calculate the noise in the rest frame of the particle, where the discretized version of the Langevin equation (1.1) is
\[
M \Delta \nu / \epsilon = \eta.
\]  
(2.14)

The desirable fluctuation dissipation theorem that the noise is expected to satisfy then reads in discrete form as
\[
\langle \eta_i \eta_j \rangle = 2k_B T \Gamma \delta_{ij}/\epsilon
\]  
(2.15)

Note, that the function \(\delta(t_i - t_j) \rightarrow \delta_{ij}/\epsilon\), such that for \(i = j\), \(\delta(0) \rightarrow 1/\epsilon\), which is the appropriate discrete form (17). This is the relation we will now derive from the kinematics of the collisions between the Brownian particle and the gas molecules. The momentum along \(x\), transferred to B in the interval \(\epsilon\) is \(\eta\), which we call \(\delta p_x\). We have to show that:

- The momentum transferred \(\delta p_x\) is distributed independently in each time interval \(\epsilon\).
- The mean square value of \(\delta p_x\) in any given time is given by
\[
\langle (\delta p_x)^2 \rangle = 2k_B T \Gamma \epsilon
\]  
(2.16)

The first of the above statements follows from the fact that the gas is ideal, so that each collision is independent and the coarse graining over time will obviously not generate correlations. Suppose a total of \(N\) collisions take place in the interval \(\epsilon\), counting all velocities. The total momentum transferred is
\[
\delta p_x = m(1 + \kappa)(v_{x1} + ... + v_{xN})
\]  
(2.17)

Once again, since the velocities are independent, all cross terms have a zero average, leading to
\[
\langle (\delta p_x)^2 \rangle = m^2(1 + \kappa)^2 N \langle v_x^2 \rangle
\]  
(2.18)

The number of particles of velocity \(v\) that collide in time \(\epsilon\) is
\[
N(v) = \frac{\rho}{m} A e P_0(v)|v_x|
\]  
(2.19)
The total number of collisions is most easily calculated in Cartesian coordinates:

\[
N = A \frac{\rho}{m} \epsilon \int d\mathbf{v} P_c(\mathbf{v})|v_x|
\]

\[
= 2A \frac{\rho}{m} \sigma \chi_3 + \mathcal{O}((u_0/\sigma)^2) \quad (2.20)
\]

A calculation in polar coordinates to the leading order gives

\[
N = A \frac{\rho}{m} \sigma \chi_3 \quad (2.21)
\]

which is the same result as \(\chi_3/\chi_1 = 2\) (as shown in Appendix B). The average \(\langle v_x^2 \rangle\) is not the thermal average, but the average over the sample of particles that collide with \(B\) in the interval \(\epsilon\).

\[
\langle v_x^2 \rangle = \frac{1}{N} \frac{\int d\mathbf{v} N(\mathbf{v}) v_x^2}{\int d\mathbf{v} N(\mathbf{v})} = \frac{1}{N} A \frac{\rho}{m} \epsilon \int d\mathbf{v} P_c(\mathbf{v}) v_x^2 |v_x|
\]

\[
= \frac{1}{2\sigma \chi_3} + \mathcal{O}((u_0/\sigma)^2)
\]

\[
\simeq 2\sigma^2 \quad (2.22)
\]

Note that the mean square velocity in Eqn. (2.22) is larger than the thermal average velocity \(\sigma^2\). This is due to the fact that in the ensemble of molecules that collide in a given interval, there are a greater number of faster molecules, as they sweep a larger cylinder (Figure 2). Substituting for \(N\) and \(\langle v_x^2 \rangle\) in equation (2.18) we get

\[
\langle (\delta p_x)^2 \rangle = m^2 (1 + \kappa)^2 A \frac{\rho}{m} \sigma \chi_3 \sigma^2 \quad (2.23)
\]

Combining equations (2.23) and (2.12) and using equations (2.6) and (B2) the above equation becomes

\[
\langle (\delta p_x)^2 \rangle = (1 + \kappa)k_B T \Gamma \epsilon \quad (2.24)
\]

which for \(\kappa = 1\), i.e. for \(M >> m\) goes to the desired fluctuation dissipation result (2.16). Also note that the change of momentum (or velocity) of the Brownian particle, in a time step \(\epsilon\), is of the order \(\sqrt{\epsilon}\) and not \(\epsilon\), which might be naively expected. This is an essential feature of Langevin equation [17].

### III. BROWNIAN MOTION IN AN IDEAL GAS WITH SMALL MEAN FREE PATH

The classical ideal gas is a familiar concept, described by the equation of state

\[
P V = n R T. \quad (3.1)
\]

This equation of state is a limiting case of a more physically reasonable equation of state, namely the real gas (Van der Waals gas) equation ([18])

\[
(P - \frac{a}{V^2})(V - b) = n R T. \quad (3.2)
\]

where \(a\) and \(b\) represent the intermolecular forces and the volume occupied by the gas molecules respectively. The physical meaning of working in the ideal gas limit corresponds to neglecting all forces between the particles other than the two body hard sphere collisions, and neglecting the volume occupied by the molecules themselves as compared to the volume of the gas.

It turns out that there is no unique way of reaching such a limit and different limiting procedures lead to different physical situations. One way is to make the gas more and more dilute in the hope that it will finally become ideal. As a consequence of dilution, the collision rate is reduced and finally goes to zero while the mean
free path approaches infinity. Though such a gas will satisfy the ideal gas equation of state, it will have infinite relaxation time, and will never equilibrate on its own! However, once the equilibrium is established it is maintained in the absence of external perturbations. This is the kind of gas we considered in section IV for the passage of a Brownian particle through it.

The second way is more interesting, in that one can consistently carry out the limiting process from a real gas to an ideal gas while retaining a finite collision rate. In fact it is possible to fix the collision rate at any desired value and go through the limiting procedure. As a consequence we can make the relaxation time as small as we wish. Therefore, if disturbed from equilibrium, such a gas will equilibrate on its own.

Both these cases correspond to different physical situations and the behaviour of a Brownian particle injected in either of the gases is very different in each case.

Going back to the motion of a Brownian particle in second type of gas we observe that the relaxation time (the time in which the gas goes back to equilibrium, after being disturbed) can be made smaller than the coarse graining time (the time for which the Brownian particle does not change its velocity appreciably). In fact we are allowed to assume any preassigned value for the relaxation time and other parameters can be adjusted accordingly. The picture of the previous case where we assumed that the gas is practically collisionless (at least within coarse graining time $\epsilon$) is no longer valid. The number of gas particles colliding with the Brownian particle per unit time at velocity $v$ is no longer the number of particles in the slanted cylinder of height $v_x$, as the particles keep colliding and forgetting their velocities within the time $\epsilon$.

It turns out that it is simpler to compute the collision rate in this case as we do not have to worry about the slanted cylinder. The gas particles colliding with the Brownian particle are chosen randomly from a continuously equilibrating velocity distribution, as seen from the rest frame of the Brownian particle. The memory effect present in the slanted cylinder description of the previous section disappears. The number of collisions per unit time $N(v)$ of the gas molecules moving with a velocity $v$ with the Brownian particle in this case (Figure 3) is

$$N(v) = K \frac{\rho}{m} A v_{th} P(v). \quad (3.3)$$

where $v_{th} = \sqrt{\frac{k_B T}{m}}$ is the thermal velocity, $K$ is a normalisation constant and all other parameters have the same meaning as in eq. (2.19). The average force can now be readily obtained as in the previous case

$$F = \int N(v) \delta p dv. \quad (3.4)$$

Using the value of $\delta p$ from the equation (2.2) and of $N(v)$ from eqn. (3.3) we have

$$F = K(1 + \kappa)\rho A v_{th} \int P(v) v dv$$

$$= -w_0 \Gamma \quad (3.5)$$

where the friction coefficient $\Gamma = k(1 + \kappa)\rho A v_{th}$. It is interesting that the friction being proportional to the velocity of the Brownian particle is an exact result here.

We now move on to the noise calculation, the treatment being very similar to that of section II. The momentum transferred in each time $\epsilon$ is obviously independent and we basically only have to show that $\langle p^2 \rangle = 2k_B T \epsilon$. The equation (2.18) is still valid for the Brownian plate where only the $x$ component of momentum is important but the expressions for the total number of collisions $N$ and $\langle v_x^2 \rangle$ are different in this case. We have for the Brownian particle at rest

$$N = \int N(v) dv$$

$$= K \frac{\rho}{m} A v_{th} \quad (3.6)$$

and since there are no memory effects we have the pure thermal velocity distribution with

$$\langle v_x^2 \rangle = \frac{k_B T}{m} \quad (3.7)$$

Using these expressions and the equation (2.18) we get

$$\langle p_x^2 \rangle = m^2(1 + \kappa)^2 K \frac{\rho}{m} A v_{th} \epsilon \frac{k_B T}{m}$$

$$= (1 + \kappa)k_B T \epsilon \quad (3.8)$$

In the limit when Brownian particle is of large mass compared to the gas molecules i.e. $\kappa \to 1$ we recover the fluctuation dissipation theorem (2.16). The derivation has been simpler and more exact in this case, where the gas is constantly equilibrating. We have not used any approximations here as opposed to Section II. It is also clear in this case that the separation of time scales for the motion of the gas molecules and that of the Brownian particle is essential for the fluctuation dissipation theorem to hold and thus the theorem is valid only in the limit of $\kappa \to 1$.

IV. CONCLUDING REMARKS

We have shown, how the familiar result of Langevin equation and fluctuation dissipation theorem can be derived and understood in a special case when the fluid through which the Brownian particle moves is an ideal gas. The frictional force comes about because of the fact that if $B$ moves in a particular direction then as seen from the frame of $B$ the velocity of gas molecules hitting it from the front is more compared to that for the molecules hitting it from behind. As the details of the calculations in section II and III show, the situation is a little more subtle and we have to be careful while setting up the expression for the collision rate as a function of velocity. Moreover, the separation of time scales for the motion of the Brownian particle and the gas particles is essential for obtaining the fluctuation dissipation theorem.
As a matter of contrast we observe that the essential difference in the two kind of ideal gases is in the distribution \( N(v) \) of collision rate at velocity \( v \). For the ideal gas of the first kind, this function tends to have larger values for larger velocities as compared to the Maxwellian, as the volume of the cylinder from which all the molecules must collide with \( B \) is directly proportional to \( |v| \). On the other hand, for the ideal gas of the second type, the absence of memory effects and the breakdown of the cylinder picture prevents any such biases.

Another interesting observation is that the friction coefficient is proportional to the cross-section area for both the cases of the plate and the sphere unlike in the case of Stokes’ law where it is proportional to the radius. This is due to the fact that we have neglected the back reaction due to the motion of the sphere on the velocity distribution of the gas particles, which has been retained to be Maxwellian all along. On the contrary for the calculation of the Stokes’ law one takes into account the effect of the motion of the sphere on the fluid velocity. While our treatment holds for a dilute noninteracting gas, the presence of memory effects and the breakdown of the cylindrical picture prevents any such biases.

In this appendix, we demonstrate that the friction coefficient can be calculated for the case when the Brownian particle is a sphere instead of a plate. The underlying physics is same though the calculation is a little more involved. The plate was chosen only for simplicity and this calculation is given here to convince the reader that there is nothing special about the plate. We will see that the only difference from the plate case is a geometrical factor.

Imagine the Brownian particle to be a sphere of radius \( R \) moving in the \( \hat{z} \) direction with velocity \( \dot{u}_0 \). We consider a frame of reference \( F \) which is at rest with respect to the Brownian particle. Consider the collision of the Brownian particle with a beam of particles moving with velocity \( V(V, \theta', \phi') \) in this frame. Further consider a frame \( F' \) again at rest with respect to the Brownian particle but with its orientation such that the \( \hat{z}' \) axis is in the direction of \( V \). When a narrow beam hits the sphere at a point \( (R, \theta, \phi) \) in the frame \( F' \), it is reflected by the sphere and the force exerted on the sphere, which is along \( \hat{z}' \) direction is given by

\[
F_{\hat{z}'} = \text{flux}(1 + \kappa) V \cos \theta \hat{z}'.
\]

Where

\[
\text{flux} = \rho V_r (-ds) = \rho V_o \cos \theta R^2 \sin \theta d\theta d\phi \quad (A1)
\]

**APPENDIX A: CALCULATION OF FRICTION COEFFICIENT FOR A BROWNIAN SPHERE**

The velocity distribution of equation \( \text{[2.7]} \) breaks the \( \theta' \) symmetry but preserves the \( \phi' \) symmetry, therefore in the frame \( F \) the \( \hat{x} \) and \( \hat{y} \) component of the force averages to zero and we need to consider only the \( \hat{z} \) component of the force.

\[
F_{\hat{z}} = F_{\hat{z}'} \cos \theta'.
\]

Rewriting the eqn \( \text{[2.7]} \) for the velocity distribution in the spherical polar coordinates as seen from the frame \( F \) we have

\[
P_r(V) = \frac{1}{(2\pi\sigma)^3} e^\left(\frac{-((V_o \cos \theta' + \dot{u}_0)^2 + (V_o \sin \theta')^2)}{2\sigma^2}\right) (A3)
\]

The total frictional force can now be readily obtained by integrating over all the angular variables and the velocity distribution

\[
F_{\hat{z}} = C_1 C_2 \int_0^{\infty} dV_o V_o^4 e^{-V_o^2/2\sigma^2} \int_0^{\pi} \frac{1}{(2\pi\sigma)^3} e^{2u_o V_o \cos \theta'/2\sigma^2} \sin \theta' \cos \theta' d\theta' (A4)
\]

where,

\[
C_1 = (2\pi)^2(1+\kappa)R^2 e^{-\frac{u_o^2}{2\sigma^2}} \quad \text{and} \quad C_2 = \int_0^{\pi} d\theta \sin \theta \cos^2 \theta = 2/3 \quad (A5)
\]

To the lowest order, the \( \int d\theta' \) gives \( \dot{u}_o V_o / 3\sigma^2 \) and by working out the \( \int dV_o \) we obtain the total frictional force

\[
F_{\hat{z}} = -C_1 C_2 \frac{\dot{u}_o \sigma}{6\pi} \chi_5 \quad (A6)
\]

![FIG. 3: A pictorial description of collisions for a spherical Brownian particle.](image)
Using the dimensionless integral $\chi_5$ from appendix B, the relation $\chi_5 = 4\chi_3$ and substituting the values of $C_1, C_2$, the final expression for the force simplifies to

$$F_Z = -\frac{8}{9} (2\rho(1+\kappa)u_o\sigma\chi_3)$$

where $A = \pi R^2$ is the cross section of the sphere. We notice that the only difference in this expression as compared to the plate case of eqn. (2.11) is the geometrical factor of $8/9$.

APPENDIX B: SOME USEFUL INTEGRALS

We list some useful integrals used in the paper.

$$\Gamma(n) = \int_0^\infty dx x^{n-1} e^{-x} = 2 \int_0^\infty dx x^{2n-1} e^{-\frac{x^2}{2}}$$

$$\chi_n = \frac{1}{\sqrt{2\pi}} \int_0^\infty dx x^{n-1/2} e^{-\frac{x^2}{2}} = \frac{1}{\sqrt{2\pi}} 2^{n-1/2} \Gamma \left( \frac{n+1}{2} \right)$$

$$\chi_3/\chi_1 = 2 \quad \chi_5/\chi_3 = 4$$

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