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Sedimentation of Brownian Particles in a Gravitational Potential

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The settling of a Brownian particle in a semi-infinite fluid bounded by a bottom plane is studied on the basis of Smoluchowski's exact solution of the equation describing diffusion in the gravitational potential. Expressions are derived for the mean height and the variance of height at some time after starting at an initial height. These quantities show interesting behavior as a function of time. It is shown that for certain initial heights the Boltzmann entropy does not increase steadily. It increases at first but then decreases to its equilibrium value.

KEY WORDS: Brownian motion; sedimentation; gravitational potential; entropy.

1. INTRODUCTION

The settling of a Brownian particle in a semi-infinite fluid bounded by a horizontal bottom plane provides an illuminating application of the theory of stochastic processes. The problem was studied by Smoluchowski,[1] who gave an exact solution of the equation describing diffusion in a gravitational potential. He derived an expression for the conditional probability of finding the particle at a certain height after starting at a different height at an earlier time. The problem was studied independently by Mason and Weaver,[2] who solved the same equation for some special initial density profiles. Smoluchowski's solution was discussed by Chandrasekhar[3] in his well-known review, but he did not add to Smoluchowski's work. A wealth of information is hidden in the complex fundamental solution found by Smoluchowski. In the following we discuss some of its striking features.

Dedicated in friendship to Professor J. Robert Dorfman on the occasion of his sixty-fifth birthday.

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In particular we study the mean height and its variance as a function of time. Smoluchowski[1] took the mean height to be a measure of the entropy. In particular he considered a particle starting at the bottom, and achieving a mean equilibrium height after a long time. Since the latter is above the starting-point he argued that this implies a decrease of entropy, though adding that this does not allow the construction of a perpetuum mobile. Smoluchowski's view was repeated by Chandrasekhar.[3,4] Actually we shall see that for the situation considered the entropy, properly defined à la Boltzmann, steadily increases. On the other hand there are other situations for which the entropy first increases, and then decreases to its equilibrium value. We also study the probability to be above the mean height after starting out at some initial height, and find curious behavior.

The probability distribution of the time of first hitting the bottom after release from a specified height is given by a rather simple expression[5,6] and will not be discussed further. It is worth noting that the first-passage-time density, as well as the mean recurrence time, has also been calculated on the basis of the Fokker-Planck equation describing the diffusion and drift in velocity space.[7]

A solution similar to that of Smoluchowski has been found for Lamm's equation, which describes centrifugal sedimentation.[8] This solution should imply features similar to those found here for the gravitational case.

2. ORIENTATIONAL TIME-CORRELATION FUNCTIONS

We consider a Brownian particle of mass m, diffusion coefficient D, located in the half-space $z > 0$ and in the presence of a gravitational potential $\phi(\mathbf{r}) = mgz$. The particle is reflected at the bottom plane $z = 0$. The diffusion in horizontal directions is identical to that of a free particle, and can be omitted from consideration. Integrating over horizontal coordinates we find that the conditional probability distribution $P(z \mid z_0, t)$ for the vertical coordinate z for time $t > 0$ satisfies the Smoluchowski equation

$$\frac{\partial P}{\partial t} = D\left[\frac{\partial^2 P}{\partial z^2} + \frac{mg}{kT}\frac{\partial P}{\partial z}\right] \tag{2.1}$$

with initial condition $P(z \mid z_0, 0) = \delta(z - z_0)$. The explicit solution was given by Smoluchowski.[1] In dimensionless form Eq. (2.1) reads

$$\frac{\partial P}{\partial t} = \frac{\partial^2 P}{\partial z^2} + \frac{\partial P}{\partial z}. \tag{2.2}$$

From the solution of this equation one can reconstruct the solution of Eq. (2.1) by replacing z by κz with $\kappa = \sqrt{kT/mg}$ and t by $D\kappa^2 t$. For brevity of notation we indicate the initial coordinate by y rather than z_0. The reflection at $z=0$ implies the boundary condition

$$\left.\frac{\partial P(z \mid y, t)}{\partial z}\right|_{z=0} + P(0 \mid y, t) = 0. \tag{2.3}$$

Smoluchowski's solution reads

$$P(z \mid y, t) = \frac{1}{2\sqrt{\pi t}}\left[\exp\left[-\frac{(z-y)^2}{4t}\right] + \exp\left[-\frac{(z+y)^2}{4t}\right]\right]\exp\left[-\frac{z-y}{2} - \frac{t}{4}\right]$$
$$+ \frac{1}{2} e^{-z} \operatorname{erfc}\left[\frac{z+y-t}{2\sqrt{t}}\right]. \tag{2.4}$$

The solution reduces to $P(z \mid y, 0+) = \delta(z-y)$ at short times, and tends to the equilibrium distribution

$$P_{\mathrm{eq}}(z) = \exp(-z) \tag{2.5}$$

as t tends to infinity. The solution is to be compared with that valid in the absence of the bottom wall,

$$P_0(z \mid y, t) = \frac{1}{2\sqrt{\pi t}} \exp\left[-\frac{(z-y+t)^2}{4t}\right] \tag{2.6}$$

holding for all y, z. This does not tend to an equilibrium solution as $t \to \infty$.

In order to obtain the solution Eq. (2.4) Smoluchowski transformed the Eq. (2.2) to the free diffusion equation for $\psi(z \mid y, t) = \exp\left(\frac{1}{2}z + \frac{1}{4}t\right) P(z \mid y, t)$. This is a special case of a more general tranformation of the Smoluchowski equation to a Schrödinger equation with imaginary time.[9] The diffusion equation in the presence of a wall can be solved by the method of images.[10, 11] The second term in Eq. (2.4) clearly corresponds to the image $-y$ of the first term with source at y. The last term can be expressed as

$$\frac{1}{2} e^{-z} \operatorname{erfc}\left[\frac{z+y-t}{2\sqrt{t}}\right] = \frac{1}{2\sqrt{\pi t}} \int_y^{\infty} \exp\left[-\frac{(z+\eta)^2}{4t} - \frac{z-\eta}{2} - \frac{t}{4}\right] d\eta \tag{2.7}$$

corresponding to a continuous distribution of sources from $-\infty$ to $-y$ along the negative z-axis.

The solution satisfies the symmetry relation

$$P(z \mid y, t)\, P_{\text{eq}}(y) = P(y \mid z, t)\, P_{\text{eq}}(z). \tag{2.8}$$

In particular it follows from Eq. (2.8) that the average of any quantity $G(z)$

$$g(y, t) = \int_0^\infty G(z)\, P(z \mid y, t)\, dz \tag{2.9}$$

satisfies the adjoint equation

$$\frac{\partial g}{\partial t} = \frac{\partial^2 g}{\partial y^2} - \frac{\partial g}{\partial y} \tag{2.10}$$

with initial condition $g(y, 0) = G(y)$ and boundary condition

$$\left.\frac{\partial g}{\partial y}\right|_{y=0} = 0. \tag{2.11}$$

It was shown graphically by Smoluchowski[1] that the approach of the probability $P(z \mid y, t)$ to its equilibrium value $\exp(-z)$ need not be monotonic. In Fig. 1 we plot $P(1 \mid y, t)$ as a function of time for the three initial values $y = 1.8, 1.9$, and 2.0. This shows that for the first two cases the probability even oscillates about the final equilibrium value $1/e$. In the following we study some curious features of the approach to equilibrium in more detail.

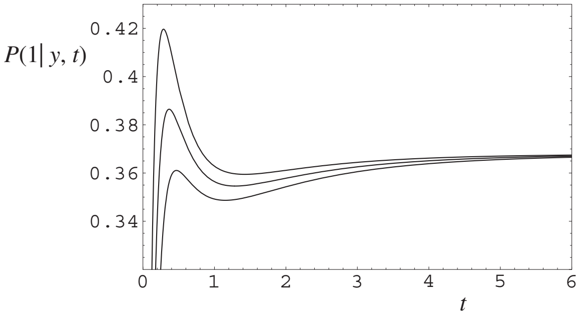

Fig. 1. Probability $P(1 \mid y, t)$ to be at the mean equilibrium height 1 at time t after starting at initial height y at time $t = 0$ for $y = 1.8$, $y = 1.9$, and $y = 2.0$ (top to bottom).

3. MEAN HEIGHT AND VARIANCE OF HEIGHT

The mean height of the Brownian particle, starting to diffuse at height y at time $t=0$,

$$M(y,t)=\int_0^\infty zP(z\mid y,t)\,dz \tag{3.1}$$

follows straightforwardly from the probability distribution Eq. (2.4). It is given by

$$M(y,t)=y-t+\frac{1}{2}(1-y+t)\operatorname{erfc}\left(\frac{y-t}{\sqrt{4t}}\right)-\frac{1}{2}e^{y}\operatorname{erfc}\left(\frac{y+t}{\sqrt{4t}}\right)+\sqrt{\frac{t}{\pi}}\exp\left[-\frac{(y-t)^2}{4t}\right]. \tag{3.2}$$

For $y\to\infty$ at fixed t this tends to the result $M_0(y,t)=y-t$ found from Eq. (2.6) in the absence of the wall. For $t\to\infty$ at fixed y the average $M(y,t)$ tends to the equilibrium value $M_{eq}(y)=1$. It can be checked that $M(y,t)$ satisfies Eq. (2.10) with boundary condition (2.11).

The behavior in time is not monotonic. At short times the average decreases as $y-t$ for any y. This shows that even for $y<1$ the average first decreases before it starts to increase. For $y=1$ the decrease is substantial. The minimum $M(1,t_{min})=0.8245$ is attained at $t_{min}=0.4676$. By continuity, for any $y>1$ the average shows a minimum below 1 before it increases. For $y=1.75$ the minimum is 0.9997 and is attained at $t_{min}=9.8840$. In Fig. 2 we show the average $M(y,t)$ for the initial values $y=0.5, 0.75, 1.0, 1.25, 1.5$, and 1.75.

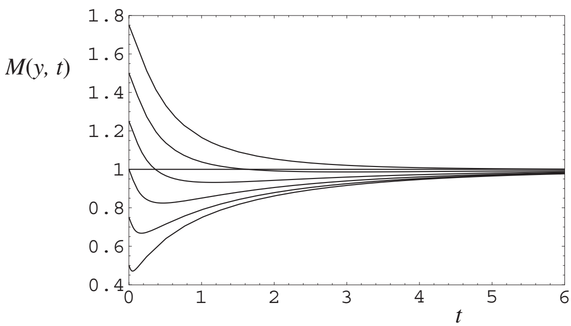

Fig. 2. Mean height $M(y,t)$ as a function of time t for initial values $y=0.5$, $y=0.75$, $y=1.0$, $y=1.25$, $y=1.5$, and $y=1.75$ (bottom to top).

Of course, the fluctuations can be large. For large positive y and for $t \ll y$ the solution (2.4) is approximated well by the solution (2.6) for absent wall. For the latter solution the variance of the height grows proportionately with time. On the other hand, for large times the distribution tends to equilibrium, so that the variance must tend to unity. The average of the squared height

$$Q(y, t) = \int_0^\infty z^2 \, P(z \mid y, t) \, dz \tag{3.3}$$

is found to be given by

$$Q(y, t) = (y-t)^2 + 2t + \left[1 - t - \frac{1}{2}(y-t)^2\right] \operatorname{erfc}\left(\frac{y-t}{2\sqrt{t}}\right) + (y+t-1)\, e^y \operatorname{erfc}\left(\frac{y+t}{2\sqrt{t}}\right) + (y-t-2)\sqrt{\frac{t}{\pi}} \exp\left[-\frac{(y-t)^2}{4t}\right]. \tag{3.4}$$

For short times $Q(y, 0+) = y^2$, and for long times $Q(y, t)$ tends to the equilibrium value $Q_{eq} = 2$. It can be checked that $Q(y, t)$ satisfies Eq. (2.10) with boundary condition (2.11). In Fig. 3 we plot the variance

$$\Delta(y, t) = Q(y, t) - M^2(y, t) \tag{3.5}$$

as a function of time for $y = 0.5$, 1.0, 1.5, 2.0, and 3.0. From the last curve it is evident that for $y \gg 1$ the presence of the bottom wall is noticeable long before $t = y$.

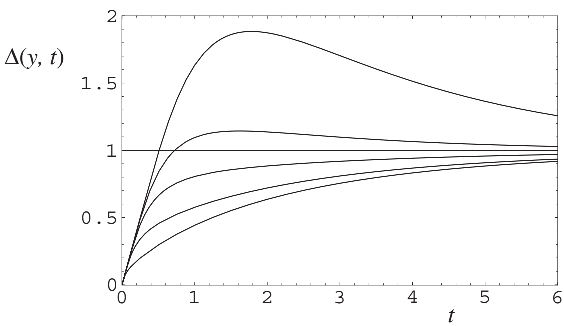

Fig. 3. Variance $\Delta(y, t)$ as a function of time t for initial values $y = 0.5$, $y = 1.0$, $y = 1.5$, $y = 2.0$, and $y = 3.0$ (bottom to top).

4. PROBABILITY TO BE ABOVE AVERAGE

As shown in Fig. 1, for certain initial values y above average, the probability to be at the average height tends to its equilibrium value $1/e$ nonmonotonically. This suggests that the same may be true for the probability to be above average. In this section we investigate the probability

$$A(y, t) = \int_1^\infty P(z \mid y, t)\, dz. \tag{4.1}$$

At the initial time this is a step-function

$$A(y, 0) = \theta(y-1). \tag{4.2}$$

At long times $A(y, t)$ tends to $1/e$ independent of y.

Substituting Eq. (2.4) into (4.1) we find that the first two terms can be integrated easily. One calculates the integral of the last term conveniently by first taking a partial derivative with respect to y. The result can be integrated over z, and subsequently the result of this can be integrated over y. The value at the boundary $y = 0$ can be found easily by integration by parts. Thus we find the probability

$$A(y, t) = \frac{1}{2}\,\mathrm{erfc}\left(\frac{1-y+t}{2\sqrt{t}}\right) + \frac{1}{2e}\,\mathrm{erfc}\left(\frac{1+y-t}{2\sqrt{t}}\right). \tag{4.3}$$

This clearly has the initial value given by Eq. (4.2) and the limiting value $1/e$. It can be checked that the function satisfies Eq. (2.10) with boundary value (2.11).

At $y = 1+$ the probability $A(1, t)$ decays below the final value $1/e = 0.3679$. Thus, even when starting just above the mean equilibrium height, the probability to be above average rapidly decreases to a minimum value 0.3266 at time $t = 0.7959$ before attaining the final value $1/e$. In Fig. 4 we plot $A(1+, t) - 1/e$ as a function of time.

It is also of interest to consider the time-evolution of the probability distribution when starting with an equilibrium distribution above the mean equilibrium height. This distribution is given by

$$B(z, t) = e \int_1^\infty e^{-y}\, P(z \mid y, t)\, dy. \tag{4.4}$$

By the symmetry Eq. (2.8) this is given by

$$B(z, t) = e^{1-z} \int_1^\infty P(y \mid z, t)\, dy, \tag{4.5}$$

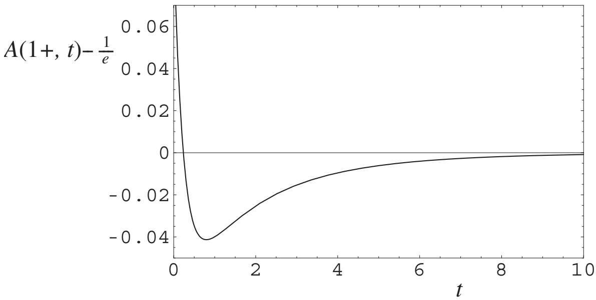

Fig. 4. Plot of $A(1+, t) - 1/e$ as a function of time, where $A(y, t)$ is the probability to be above average 1 at time t, when starting from height y at time 0, and $1/e$ is the limiting equilibrium value.

so that

$$B(z, t) = e^{1-z} A(z, t). \tag{4.6}$$

The behavior as a function of time at $z = 1$ follows from Fig. 4. In Fig. 5 we plot the distribution $B(z, t)$ as a function of z for times $t = 0.1$, 0.5, and 1.0.

5. DECREASE OF ENTROPY

In this section we discuss a dilute system of many Brownian particles. For such a system one can define a non-equilibrium entropy and free energy. We discuss the behavior of these thermodynamic quantities as a function of time. The non-equilibrium entropy per particle, when all

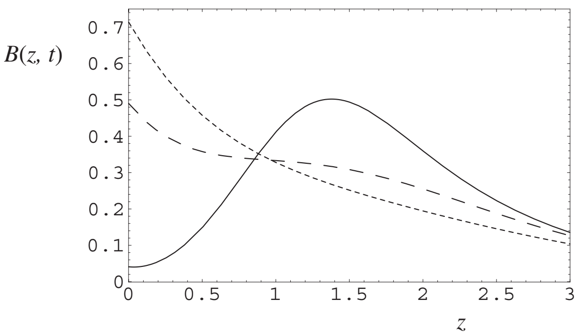

Fig. 5. Probability distribution $B(z, t)$, defined in Eq. (4.4), as a function of height z at times $t = 0.1$ (solid curve), $t = 0.5$ (dashed curve), $t = 1.0$ (dotted curve).

particles start to diffuse from height y at time $t=0$, is according to Boltzmann in dimensionless units

$$S(y,t) = -\int_0^\infty P(z\,|\,y,t)\ln P(z\,|\,y,t)\,dz. \tag{5.1}$$

The corresponding free energy is

$$F(y,t) = M(y,t) - S(y,t). \tag{5.2}$$

It can be expressed as

$$F(y,t) = \int_0^\infty P(z\,|\,y,t)\ln\frac{P(z\,|\,y,t)}{P_{\mathrm{eq}}(z)}\,dz. \tag{5.3}$$

It follows from the H-theorem for the Smoluchowski equation[12] that this is a monotonically decreasing function of time. The initial value $F(y,0+)$ is infinite, and the final equilibrium value vanishes. The average $M(y,t)$ can both increase and decrease. We have shown in Section 3 that for $y \geqslant 1$ the function first decreases, and then increases. It is natural to ask for the behavior of the non-equilibrium entropy $S(y,t)$.

The initial value of the entropy $S(y,0+)$ is minus infinity. Its final equilibrium value is unity, independent of y. However, it is clear that for sufficiently large y the entropy does not increase monotonically. As long as the influence of the wall is negligibly small the entropy increases. It can attain large positive values, but as soon as the presence of the wall is felt the entropy decreases to unity. The decrease corresponds to narrowing of the distribution function, as shown in Fig. 3. In Fig. 6 we plot the behavior

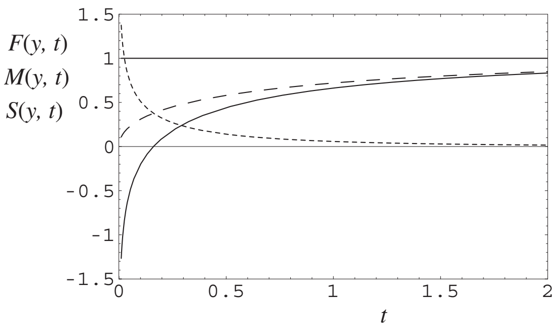

Fig. 6. Plot of free energy $F(y,t)$ (dotted curve), mean height $M(y,t)$ (dashed curve), and entropy $S(y,t)$ (solid curve) as a function of time t for initial height $y=0$.

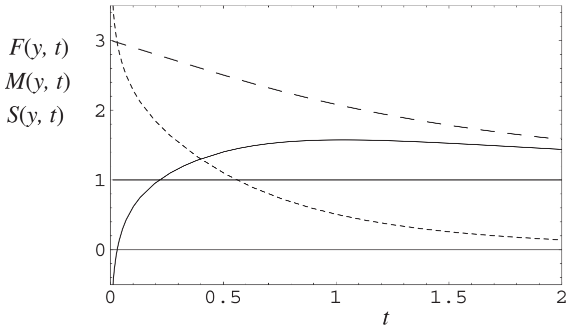

Fig. 7. Same as in Fig. 6 for initial height $y = 3$.

of free energy $F(y, t)$, potential energy $M(y, t)$, and entropy $S(y, t)$ for the initial value $y = 0$. In this case both M and S increase monotonically. In Fig. 7 we plot the behavior of these functions for initial value $y = 3$. The function $S(3, t)$ shows a maximum.

The discussion of Smoluchowski[1] and Chandrasekhar[3,4] of the behavior of the entropy is incorrect. They identified $-M(y, t)$ with the entropy. As discussed above, $-M$ can both increase and decrease. The free energy $F(y, t)$ decreases monotonically. The difference of potential energy $y-1$ is transferred to the heat bath. The entropy of the system of Brownian particles is a measure of its geometrical disorder. The gravitational potential and the bottom wall have an ordering effect.

6. DISCUSSION

We have shown that the settling of a Brownian particle in bounded plane geometry exhibits interesting features. Smoluchowski's exact solution for the conditional probability to be at a certain height incorporates a wealth of detail. We have studied in particular the mean height and the variance of height at some time after starting at an initial height. These quantities exhibit curious behavior as functions of time and initial height. We have also studied the probability to be above the mean equilibrium height after some time. Perhaps the most striking feature is the behavior of the Boltzmann entropy. We have shown that for sufficiently high initial position the entropy at first steadily increases, and then decreases to its equilibrium value.

We have not investigated the first passage-time distribution in any detail. The distribution can be evaluated easily from the Laplace-transform of the Smoluchowski equation by use of the formalism developed by Darling and Siegert.[13] If the height of passage is below the initial height, then the first passage-time distribution is not affected by the presence of the bottom wall, and is given by a simple expression.[5,6] For height of passage above the initial height the distribution is affected by the bottom wall.

REFERENCES

1. M. Smoluchowski, *Phys. Zeits.* **17**:557 (1916).
2. M. Mason and W. Weaver, *Phys. Rev.* **23**:412 (1924).
3. S. Chandrasekhar, *Rev. Mod. Phys.* **15**:1 (1943), reprinted in Selected papers on noise and stochastic processes, N. Wax, ed. (Dover, New York, 1954).
4. S. Chandrasekhar, M. Kac, and R. Smoluchowski, *Marian Smoluchowski, His Life and Scientific Work* (Polish Scientific Publishers PWN, Warsaw, 2000). This monograph contains a reprint and english translation of ref. 1.
5. R. von Mises, *Wahrscheinlichkeitsrechnung* (Deuticke, Leipzig, 1931), p. 511.
6. N. G. van Kampen, *Stochastic Processes in Physics and Chemistry* (North-Holland, Amsterdam, 1992), p. 295.
7. T. W. Marshall and E. J. Watson, *J. Phys. A* **18**:3531 (1985).
8. H. Fujita, *Foundations of Ultracentrifugal Analysis* (Wiley, New York, 1975).
9. Ref. 6, p. 279.
10. A. Sommerfeld, *Partielle Differentialgleichungen der Physik* (Verlag Harri Deutsch, Thun, 1978), p. 61.
11. D. R. Cox and H. D. Miller, *The Theory of Stochastic Processes* (Methuen, London, 1968), p. 224.
12. H. Risken, *The Fokker–Planck Equation* (Springer, Berlin, 1989), p. 135.
13. D. A. Darling and A. J. F. Siegert, *Ann. Math. Stat.* **24**:625 (1953).