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Mean square displacement for Brownian motion under a square-well potential and non-Einstein behaviour

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Abstract. We have obtained the mean square displacement for Brownian motion of particles in a fluid under a square-well potential. It is shown that for a deep well, there are short- and long-time regimes where the mean square displacement is proportional to time as well as a long intermediate transition stage. Even for a very mild case where the ratio A of the potential height to the thermal energy is 3 and its width is 5, we need time t of $10^{10}/D$ to recover Einstein's relation, which is unpractically too long where D is diffusion coefficient. In the short time regime where an escape process from the well dominates the considerably slow dynamics, the mean square displacement is approximately given by $4e^{-A}Dt$ with the exponential factor appearing in theory of chemical reactions.

In investigating the dynamic processes of a molecule immersed in liquids, we often require fundamental knowledge based on results from theory of Brownian motion. Among them, Einstein's relation on the mean square displacement for free motion is important not only for interpretations of experimental data [1, 2] but also for developments of further sophistication of theories on irreversible statistical mechanics [3, 4]. For two particles interacting with each other through a potential which is only a function of the relative distance, it is well known that the motion can be reduced to that for the centre of mass which undergoes free motion and the motion for the relative distance which can be treated as a one-body system. In this paper, to find how an attractive interaction may affect the dynamics of Brownian motion of two particles in a fluid, we introduce a square-well potential of height V_0 with a finite width u shown in figure 1. We assume the same diffusion coefficient D for motion both inside and outside the well and calculate the mean square displacement for the case of the initial position within the well. It will be shown that there exist two time regions where the mean square displacement is proportional to time t, whose proportionality coefficients are $4e^{-A}D$ and $2D$ for the short- and long-time regimes, respectively, in which $A = V_0/k_BT$ is the ratio of the potential depth V_0 and the thermal energy k_BT in which k_B and T are the Boltzmann constant and the absolute temperature. It is found that even for a mild case of $A = 3$ and $u = 5$ the time required for the latter Einstein relation is $10^{10}/D$, which is extremely slow. To indicate this long-time behaviour for an arbitrary potential, we carried out numerical calculations for the Lennard–Jones potential and found the same conclusion.

Brownian motion under a square-well potential in figure 1 can be regarded as free motion except for two points at $x = 0$ where the potential is infinitively large so that there will be no flux and at $x = u$ where the flux is continuous, while the probability densities

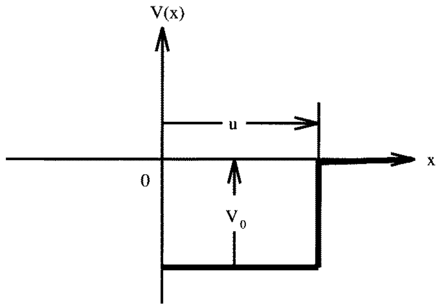

Figure 1. Square-well potential. The height and width of the potential are represented by V_0 and u, respectively.

$\rho(u-, t)$ and $\rho(u+, t)$ are discontinuous just as the potential; $\rho(u-, t) = \mathrm{e}^A \rho(u+, t)$. In view of these boundary conditions, it was shown [6] that A in [5] should be replaced by $\mathrm{e}^A - 1$, which leads to the following expression for Laplace transform of $\langle x^2(t)\rangle$,

$$L[\langle x^2(t)\rangle] = \int_0^\infty \langle x^2(t)\rangle \mathrm{e}^{-\lambda^2 t}\,\mathrm{d}t = \frac{x_0^2}{\lambda^2} + \frac{2}{\lambda^4} - 2u(\mathrm{e}^A - 1)\frac{\cosh\lambda x_0}{\lambda^3 D(\lambda)} \tag{1}$$

where

$$D(\lambda) = \cosh\lambda u + \mathrm{e}^A \sinh\lambda u \tag{2}$$

in which x_0 is the initial position of the particle at $t = 0$. We have set the diffusion coefficient $D = 1$ for brevity here. To recover the full expressions with D, we should replace t in this paper with Dt. For a relatively large value of A, and $0 \leqslant x_0 \leqslant u$, we can naturally imagine that the initial stage of the dynamics is to make the distribution of the particles uniformly in the well. The initial part of the long-time escaping dynamics of particles from the well becomes effective only after this process. Hence, instead of starting with (1) with x_0, we find it convenient to treat the case where x_0 is distributed uniformly within the well and to examine the dynamics of the escape. By taking the average with respect to x_0, we write

$$L[\Phi(t)] = L\left[\frac{1}{u}\int_0^u \langle x^2(t)\rangle\,\mathrm{d}x_0\right] = \frac{u^2}{3\lambda^2} + \frac{2\mathrm{e}^{\lambda u}}{\lambda^4 D(\lambda)} \tag{3}$$

which leads to

$$L[\Phi(t)] = \frac{u^2}{3\lambda^2} + \frac{4}{(\mathrm{e}^A + 1)\lambda^4}\left[1 + \sum_{n=1}^\infty B^n \mathrm{e}^{-2nu\lambda}\right] \tag{4}$$

where

$$B = \frac{\mathrm{e}^A + 1}{\mathrm{e}^A - 1}.$$

By taking the inverse Laplace transform of (4), we readily obtain

$$\Phi(t) = \frac{u^2}{3} + \frac{4t}{\mathrm{e}^A + 1} + \frac{4}{\mathrm{e}^A + 1}\sum_{n=1}^\infty B^n \left[(t + 2n^2u^2)\operatorname{erfc}\left(\frac{nu}{\sqrt{t}}\right) - 2nu\sqrt{\frac{t}{\pi}}\mathrm{e}^{-n^2u^2/t}\right]. \tag{5}$$

It immediately follows that for the initial stage,

$$\Phi(t) \approx \frac{u^2}{3} + \frac{4t}{e^A + 1} \tag{6}$$

whereas for the long-time approximation

$$\Phi(t) \approx \frac{u^2}{3} + 2t - 4u(e^A - 1)\sqrt{\frac{t}{\pi}} + 2u^2 e^A (e^A - 1) - \frac{2}{3}\frac{u^3(e^A - 1)(3e^{2A} - 1)}{\sqrt{\pi t}} + \frac{1}{15}\frac{u^5(e^A - 1)(15e^{4A} - 15e^{2A} + 2)}{t\sqrt{\pi t}} - O(t^{-5/2}). \tag{7}$$

It is clear that both (6) and (7) lead to Einstein's relation, $\Phi(t) = u^2/3 + 2t$ in the special case of $A = 0$. And it should be noted that both short- and long-time approximations contain terms proportional to t, originating from the diffusion process of the escape from the well and final free Brownian motion long after the escape, respectively. The latter process corresponds to Einstein's relation. We must remember that in the limit of $A \to \infty$ both expressions in (1) and (3) should lead to $u^2/3$, which corresponds to the uniform distribution within the well. Obviously (6) agrees with this, whereas (7) does not, which indicates that we cannot recover a proper limit from the long time expansion in (7). It should be noted that the escape process in (6) takes the exponential factor $\exp(-A)$ for a large value of A that appears in theory of chemical reactions and this term leads to the significantly slow dynamics, being independent of u. Whereas in equation (7), the long dynamics is characterized by a function of $\exp(A)$. Now it becomes clear that there must be an intermediate transition region where the mean square displacement, $\Phi(t) - u^2/3$ changes from $4t/(e^A + 1)$ to $2t$. To check these and what time-scale the Einstein relation dominates the dynamics, we have plotted $[\Phi(t) - u^2/3]/2t$ obtained from the first three terms on the right-hand side of equation (7) and represented by the broken curve against $\log_{10} t$ in figure 2 for a very weak condition of $A = 3$ and $u = 5$. The agreement to Einstein's relation is indicated by fitting to the top horizontal line. Even with this small value of A, we see that the Einstein relation will show up only after an extremely long time of 10^{10}. It is obvious that larger values of A and u than the above shift the time-scale to the longer side. In figure 2, we also plotted $[\Phi(t) - u^2/3]/2t$ obtained numerically (the full curve). We see a good agreement of the full curve with the broken one at long time. In the short time scale, we see the agreement with (6), which requires to fit to the bottom horizontal line. To confirm that this kind of profile is not only for the square-well potential, but also for an arbitrary interparticle potential, we carried out numerical analyses, obtained the mean square displacement of particles in three-dimensional space under the following Lennard–Jones potential and plotted $[\langle r^2(t)\rangle - r_0^2\rangle]/6t$ in figure 3

$$V(r) = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right] \tag{8}$$

where r is the interparticle distance in three dimension. In calculating the result in figure 3, we have set $(4\epsilon/k_B T) = 50$, $\sigma = 1$, $r_0 = 1.15$ and we imposed the infinitively high potential at $r = 1$. The full curve is obtained numerically and crosses are theoretical values whose details will be published elsewhere.

A new implication from the present work is to determine the potential barrier V_0 from the short-time behaviour of the mean square displacement through (6) by the light scattering experiments, for example [1, 2]. We have assumed that the potential is rigid during the whole time scale. However, it is interesting to introduce a fluctuating potential with respect

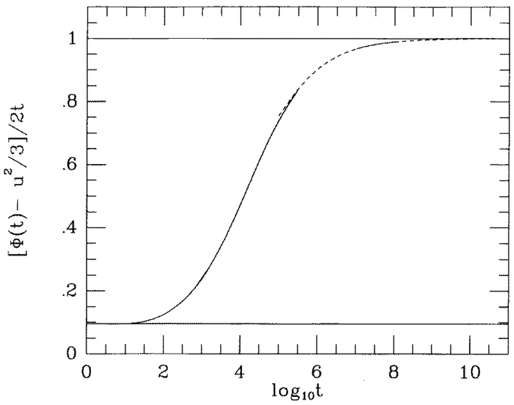

Figure 2. Plots of $[\Phi(t) - u^2/3]/2t$ versus $\log_{10} t$ for $A = 3$, and $u = 5$. The broken and full curves are obtained using the first three terms in (7) and numerical calculations, respectively. The top and bottom horizontal lines are for Einstein's relation and (6), respectively.

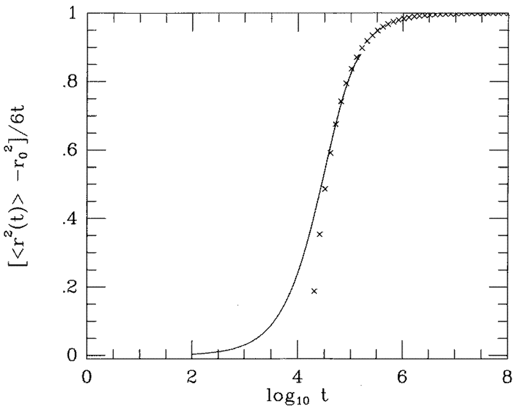

Figure 3. Plot of $[\langle r^2(t)\rangle - r_0^2\rangle]/6t$ for three-dimensional spherically symmetric Brownian motion under the Lennard–Jones potential versus $\log_{10} t$.

to time or space and to find the dynamics of the motion as a further modification of the present work.

Finally, it would be worthwhile describing how we obtained numerical results in figure 2. The following Smoluchowski equation for the probability density $\rho(x, t)$:

$$\frac{\partial\rho(x,t)}{\partial t} = \frac{\partial^2\rho(x,t)}{\partial^2 x} \tag{9}$$

can be turned into the following difference equations based on the Crank–Nicolson implicit method [7]:

$$q\rho_{i-1,j+1} - (1+2q)\rho_{i,j+1} + q\rho_{i+1,j+1} = -q\rho_{i-1,j} - (1-2q)\rho_{i,j} - q\rho_{i+1,j} \tag{10}$$

where $q = \Delta t/2(\Delta x)^2$, $t = j\Delta t$ and $x = i\Delta x$. We introduced the perfectly reflecting boundary conditions at $x = 0$ and $x = L$ so that

$$\rho_{0,j+1} = \rho_{1,j+1} \qquad \rho_{N+1,j+1} = \rho_{N,j+1}$$

where N is the end point at $x = L = N\Delta x$ which is taken to be so large that it no longer affects the dynamics. We omit describing the boundary conditions for $\rho_{i,j}$, because they are the same for $\rho_{i,j+1}$. If we represent the position of the right well at $x = u = M\Delta x$ by M, the potential must leap abruptly from M to $M+1$. Since the number of particles in $0 \leqslant x \leqslant L$ must be conserved, it follows that

$$\rho^-_{M+1,j+1} = \rho_{M+1,j+1} + (1 - \mathrm{e}^{-A})\rho_{M,j+1}$$
$$\rho^+_{M,j+1} = \mathrm{e}^{-A}\rho_{M,j+1}.$$

These relations are also valid for j, where $\rho^-_{M+1,j+1}$ and $\rho^+_{M,j+1}$ are for $i = M$ and $i = M+1$ in equation (10) in which

$$q\rho_{M-1,j+1} - (1+2q)\rho_{M,j+1} + q\rho^-_{M+1,j+1} = -q\rho_{M-1,j} - (1-2q)\rho_{M,j} - q\rho^-_{M+1,j}$$
$$q\rho^+_{M,j+1} - (1+2q)\rho_{M+1,j+1} + q\rho_{M+2,j+1} = -q\rho^+_{M,j} - (1-2q)\rho_{M+1,j} - q\rho_{M+2,j}$$

respectively. These four boundary conditions together with (10) enable us to calculate $\rho(x,t)$ numerically.

Finally let us conclude this paper by stating that there are mainly three stages in the dynamics for the deep well. The very initial stage whose dynamics is governed by the escape process from the potential similar to that for chemical reactions as given by (6) then there is a long intermediate step partially described by (7). Only at very long last, the dynamics is taken over by Einstein's relation. But we sometimes have to wait for an unreasonably long time as seen in figure 2.

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