Long-time self-diffusion in disordered media

Laia González
Facultat de Física, Universitat de Barcelona, Diagonal 645, 08028 Barcelona, Spain.[*]

Long-time self diffusion coefficient is calculated over a broad range of densities from computer simulations of a two-dimensional system obeying Brownian dynamics and interacting through a Yukawa pairwise potential. The behavior of the diffusion under changes of strength of the potential and density of particles is discussed and compared with bibliographical results. Furthermore, the effects of an external driving force and the presence of fixed particles are also considered. It is found that the diffusion lowers with the density of particles, the strength of the potential and the presence of fixed particles. On the contrary, an external force favors the diffusion. Despite the effect of the external force, a jammed state can be reached if density and proportion of fixed particles are high enough.

I. INTRODUCTION

The diffusion of a system through disordered media is strongly affected by the presence of obstacles, as well as by the density of the system or the presence of an external force.

It is of special scientific interest the phenomena of clogging, when the flow of discrete particles passing through a bottle neck is interrupted. Recent investigations have found that the probability distribution of time lapses follow a power-law tail, although a systematic study of clogging has not been carried out yet ([5]). This can be observed in systems such as suspensions of colloidal particles, polymers or particles in a gel or a solution and it can even be extended to macroscopic systems such as a crowd going out during an emergency situation, assemblies of grains or the traffic flow.

Particles passing through a bottleneck could be generalized to the case of a diffusing system under an external force where fixed obstacles are introduced. Making the amount of obstacles large enough, each of the spaces left between neighboring obstacles acts as a bottleneck.

Before getting to this point, the behavior of the diffusion coefficient needs to be studied. The system is much easily modeled by numerical simulations, given the difficulty of considering all the interactions in analytical models. We present in this paper the results of simulation of Brownian dynamics where the inter-particle interaction has been modeled by a Yukawa potential.

In a first part, the evolution of the diffusion coefficient with the density for different strengths of the interaction potential is presented and the results are compared with bibliographical data. In a second part, we give results for the diffusion when an external force and fixed particles are added.

[*]Electronic address: lgonzame10@alumnes.ub.edu

II. BROWNIAN DYNAMICS

Brownian dynamics is a model to describe the movement of large particles surrounded by a large amount of much smaller particles. The effect of the smaller particles upon the solution are described by a combination of frictional terms and random terms by the Langevin equations.

$$\dot{\mathbf{p}}(t) = -\xi\mathbf{p}(t) + \mathbf{f}(t) + \mathbf{R}(t) \tag{1}$$

$$\dot{\mathbf{r}}(t) = \frac{\mathbf{p}(t)}{m} \tag{2}$$

where $\mathbf{p}$ denotes the momentum, ξ is the friction constant, $\mathbf{f}(t)$ is a force derived from a potential, and $\mathbf{R}(t)$ is a random force. Langevin equation assumes the range of hydrodynamic interactions to be much smaller that the range of the inter-particle interaction, so that the they are neglected.

In Brownian dynamics, we are interested in long-time dynamics, where we can drop the momentum derivatives from Eq.(2).

$$\dot{\mathbf{r}}(t) = \frac{\mathbf{f}(t)}{m\xi} + \boldsymbol{\eta}(t) = \frac{D_0}{k_B T}\mathbf{f}(t) + \boldsymbol{\eta}(t) \tag{3}$$

The $\boldsymbol{\eta}$ is the random velocity derived from $\mathbf{R}(t)$ and it is delta correlated

$$< \eta_{i\alpha}(t)\eta_{j\beta}(0) >= 2D_0\delta(t)\delta_{ij}\delta_{\alpha\beta} \tag{4}$$

where the subindexes i, j identify the particle and α, β indicate the component. ξ is related with the short-time diffusion coefficient, D_0 by Einstein's relation

$$D_0 = \frac{k_B T}{6\pi\eta\sigma} = \frac{k_B T}{m\xi} \tag{5}$$

,where η and ξ are the viscosity and friction coefficient and σ is the radius of the particle.

III. METHODOLOGY

A. Inter-particle interaction

The simulation is computed in a finite system of variable size where periodic boundary conditions have been applied and the interaction between particles is modeled by a pairwise potential of the Yukawa's form $V(r) = U_0/re^{-r/\lambda}$

where U_0 is the strength of the potential, λ is its characteristic length range of the potential, which defines the size of the particles, and r is the distance between the two considered particles. We can define the steepness of the potential as $k = 1/\lambda$. Yukawa potential is a good approximation as far as many body interactions do not become relevant. The interaction force $\mathbf{f}(t)$ is given by the gradient of the Yukawa's potential. As it is a short range interaction, we have just considered its effects when $r < r_c$, and made $r_c = 3\sigma$, where σ is the particle diameter. This discontinuity at $r = r_c$ could have caused unexpected results, so a linear term was added to make the force continuous. The resulting interacting potential is

$$V(r) = U_0\left(\frac{1}{r}e^{-r/\lambda} + br\right) \tag{6}$$

with $b = \frac{1}{r_c}e^{-r_c/\lambda}(1/\lambda+1/r_c)$. The potential is measured in units of k_BT, and the force of $k_BT\sigma^{-1}$

B. Implementation

Numerical integration of (3) leads to the following algorithm ([1]), which we have introduced in our simulation.

$$\mathbf{r}(t+\Delta t) = \mathbf{r}(t) + \frac{D_0}{k_BT}\mathbf{f}(t)\Delta t + \mathbf{\Delta r^G} \tag{7}$$

where each component of $\mathbf{\Delta r^G} = \boldsymbol{\eta}\Delta t$ is a random number from a Gaussian distribution with zero mean and variance

$$< (\Delta r^G_{i\alpha})^2 >= 2D_0\Delta t \tag{8}$$

A characteristic time scale is provided by D_0, given by $\tau_B = \sigma^2/D_0$, that together with a characteristic length scale given by σ, the diameter of the particle, allows us to work with non-dimensional magnitudes.

The initialization of the particles positions was done at random in the considered two dimensional volume, so the system needed a time to thermalize, which has typically between $0.2\tau_B$ and $2\tau_B$. We started computing the average quantities after this equilibration period and the run was of $6\tau_B$. The densities were defined as the number of particles per volume unit $n = N/(l_xl_y)$, where l_x, l_y are the lengths of the box and N the number of particles in the simulation. n is given in units of σ^{-2}.

The time step has been chosen small enough so that the average square displacement per particle does not diverge, but as large as possible to reduce the simulation time. It depends on the strength of the potential chosen, as well as the particles density. For weaker potentials it was of $10^{-4}\tau_B$, but densities higher that $0.6\sigma^{-2}$ for $U_0 = 30$ and all densities for $U_0 > 30k_BT$ required to reduce Δt to $10^{-5}\tau_B$.

The size of the system has been changed so that the number of particles was of 1000 for all densities, so that we have the same statistical error.

The collective motion of the system is described by its long-time diffusion coefficient D. It is defined as the half of the slope of the average squared displacement per particle with time.

$$D = \lim_{t\to\infty}\frac{1}{2dt}\left[\frac{1}{N} < \sum_{i=1}^{N}(r_i(t) - r_i(0))^2 >\right] \tag{9}$$

, where d is the spatial dimension, we use $d = 2$. When there is no interaction between particles, D coincides with the short-time diffusion coefficient D_0. Thus, D can be obtained from the slope of the linear regression, mean squared displacement in front of the time, and the statistical error is given by the coefficient of variation, which is the ratio of the standard deviation of the mean squared displacement respect to the fit to the mean. The behavior of the diffusion coefficient is difficult to predict by analytical methods, but it has been found that the interaction between particles hinders the motion, so D/D_0 becomes smaller when the strength of the interactions or the density increase.

C. Fixed particles and external force

When a constant external force, f_{ext}, is introduced, the isotropy of the system is broken, and there is an average displacement in the $\hat{x}$ direction. Thus, some considerations need to be taken on account. For a single diffusing particle, where there are no interactions, the equation of motion (3) becomes

$$\dot{\mathbf{r}}(t) = \frac{\mathbf{f}_{ext}(t)}{m\xi} + \boldsymbol{\eta}(t) \tag{10}$$

, where $\boldsymbol{\eta}$ satisfies Eq.(4). When the equation of motion is integrated, we obtain, assuming f_{ext} in the $\hat{x}$ direction

$$\Delta x(t) = x(t) - x(0) = \frac{f_{ext}}{m\xi} + \int_0^t \Delta r^G(t')dt' \tag{11}$$

and the same but without the f_{ext} term for y.

Using the fact that $\mathbf{\Delta r^G}$ is delta correlated (Eq.(8)) and that it has a zero mean, we expect to find a dependence of the mean square displacement per particle as follows

$$\begin{aligned}
&< \Delta x >^2 = \left(\frac{f_{ext}}{m\xi}\right)^2 + \\
&\quad \int_0^t dt_1 \int_0^t dt_2 < \Delta r^G(t_1)\Delta r^G(t_2) > + \\
&\quad \frac{2f_{ext}}{m\xi}t \int_0^t < \Delta r^G(t') > = \left(\frac{f_{ext}}{m\xi}t\right)^2 + 2D_0 t \\
&< \Delta y >^2 = 2D_0 t \\
&< \Delta r >^2 = \left(\frac{f_{ext}}{m\xi}t\right)^2 + 4D_0 t \qquad (12)
\end{aligned}$$

This is an exact result for a single particle, but if we want to do the same for an interacting system, we find the effects of the interactions difficult to calculate analiticaly. However, the single particle model can be extended to an interacting system as far as the mean square displacement per particle in front of the time accepts a parabolic fit, $y = ax^2 + b$. Then, the quadratic term is related to the external force and an effective mobility, $1/(m\xi)$, while the lineal term gives the effective diffusion coefficient

$$D = b/4 \qquad (13)$$

The statistical error is given by the coefficient of variation of the fit.

Then, some fixed particle are introduced. Since there is a neat movement in the $\hat{x}$ direction due to the external force, the fixed particles apply an opposite force, on average, dispersing the particles in all directions. Hence, the diffusion coefficient will be diminished.

We consider the fixed particles to interact with the rest with the same potential (Eq.(6)). The proportion of fixed particles is defined as the number of fixed particles over the total number of particles in the box, N_{fix}/N_{tot}, and the density is calculated in terms of the total amount of particles, $n = N_{tot}/(l_x l_y)$.

The parameters of the simulation needed to be readjusted. The time step used was $\Delta t = 10^{-4}\tau_B$ for all proportions but for $N_{fix}/N_{tot} = 0.9$, when it had to be reduced to $10^{-5}\tau_B$. The number of moving particles was fixed to 1000, so the total number of particles was readjusted for each proportion. In the case of $N_{fix}/N_{tot} = 0.9$, since the total amount of particles was very large and the interaction between moving particles not so frequent we reduced it to 500.

IV. RESULTS

A. Inter-particle interaction

Results for the diffusion coefficients for a system of interacting particles with a Yukawa potential of different characteristic intensity are summarized in Fig.(1). The density is given in σ^{-2}, the diffusion coefficient in units of D_0 and strength of the potential in U_0/k_BT, all of them dimensionless. Diffusion coefficients have been obtained according to Eq.(9), and coeficients of variation for the regressions are between 2% and 7%, being higher for strong potentials.

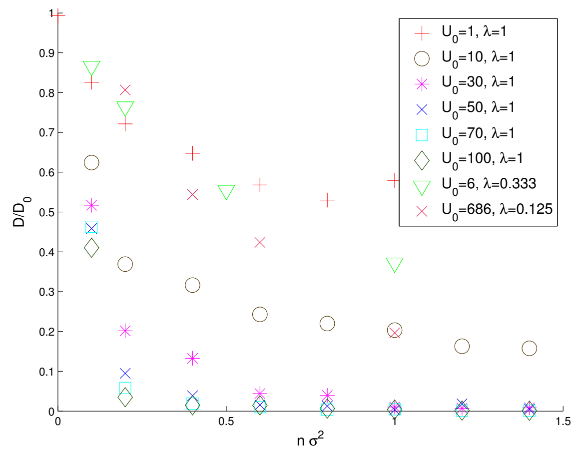

FIG. 1: Self-diffusion coefficient in terms of its low-density limit D/D_0 as a function of the density $n\sigma^2$ for a two-dimensional suspension interacting with pairwise Yukawa potential.

In the Fig.(1), we see that the diffusion coefficient decreases with the density of particles. It drops fast for lower densities and then it becomes almost constant. For stronger potentials, this shape is sharper and the diffusion coefficient lower for all densities. When U_0 is higher than $30k_BT$, a jammed state is reached for high enough densities, where the diffusion coefficient goes to zero.

In Fig.(2), the results of our own simulations and the ones carried out by H. Löwen and G.Szamel ([3]) are put together. Their definition of the Yukawa potential was slightly different, so some relations between its parameters needed to be applied.

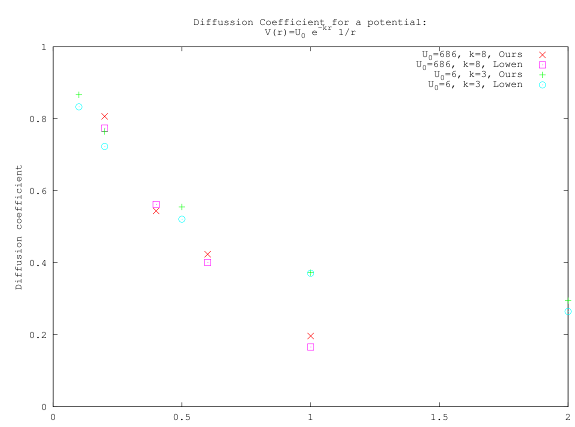

FIG. 2: The same as in Fig.(1) but now for one steeper potential, $U_0/k_BT = 686$, $k = 8\sigma^{-1}$ and one softer potential, $U_0/k_BT = 6$, $k = 3\sigma^{-1}$. Comparison between our own simulation and H. Löwen and G.Szamel results.

The obtained diffusion coefficients in our simulations are very similar of theirs, with a maximum discrepancy of 0.033 at $n\sigma^2 = 0.2$ for $U_0/k_BT = 0.2$ and $n\sigma^2 = 0.041$ for $U_0/k_BT = 0.2$, which correspond to relatives discrepancies of 6% and 4% respectively.

B. Fixed particles and external force

All the simulation in this part are done with a Yukawa pairwise interaction potential of parameters $U_0/k_BT = 10$, $\lambda = 1$.

The parabolas obtained when an external force of $0.1k_BT$ is introduced is shown in Fig.(3).

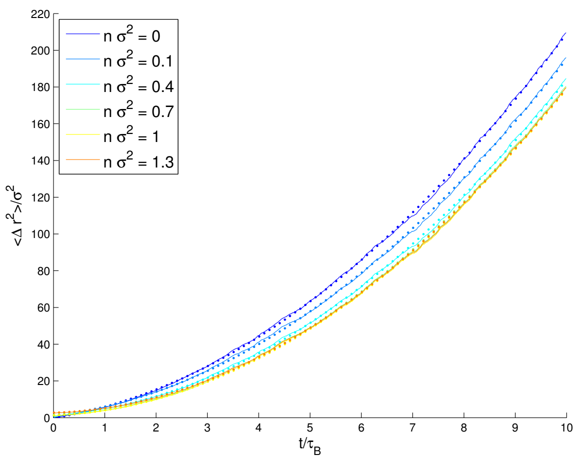

FIG. 3: Mean square displacement per particle, $<\Delta r^2> /\sigma^2$ in function of time, t/τ_B, both of them dimensionless. External force of $0.3k_BT\sigma^{-1}$ and parameters $U_0/k_BT = 10$, $\lambda = 1$ for the Yukawa interacting potential. Different densities $n\sigma^2 = 0, 0.1, 0.4, 0.7, 1$ and 1.3 are represented in colors from blue to red respectively. The dotted lines correspond to the parabola fit.

When there is no interaction between particles, which is when $n\sigma^2 = 0$ in the legend of the plot, we expect to adjust parabolas to the mean square displacement per particle according to Eq.(12). In Table I we compare the expected values with the obtained from the adjust for different external forces.

f_{ext}/k_BT	expected	obtained	rel. disc. (%)
0.1	0.19	0.16	15
0.2	0.76	0.71	6
0.3	1.70	1.65	3
0.4	3.02	2.96	2
0.5	4.73	4.65	2

TABLE I: Expected coefficients a according to Eq.(12) and the obtained from the adjust for different external forces in the first tree rows and relative discrepancy between them in the forth. The coefficients do not have units.

The obtained values are very close to the expected ones, with relative discrepancies between 2% and 15%. When there is interaction between particles, we do not have a way to calculate the expected values for the coefficients of the fit. However, as we have seen in the preceding part, the interaction hinders the diffusion, so we expect this coefficients to be lower. This behavior is shown in Fig.(3).

The effect on the diffusion of introducing constant external forces on our original system is shown in Fig.(4). The diffusion coefficients were obtained from the parabolas fit according to Eq.(13) and they are plotted in function of the density for $f_{ext}/k_BT = 0.1, 0.2, 0., 0.4$ and 0.5. The results obtained without the external force are also included for comparison. Coefficients of variation are between 0.7% and 2%, being higher for lower external forces.

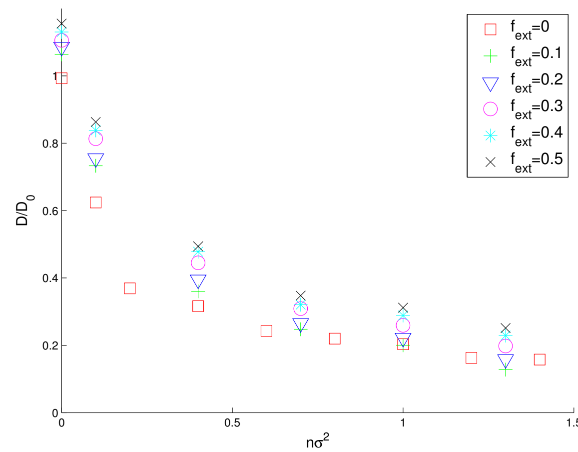

FIG. 4: D/D_0 plotted in front of $n\sigma^2$ for different external forces, of $\sigma f_{ext}/(k_BT) = 0, 0.1, 0.2, 0.3, 0.4$ and 0.5. Interaction potential of $U_0 = 10, \lambda = 1$.

When there is no interaction, the external force introduces a quadratic term to the mean square displacement due to a directional motion while the diffusion, associated to isotropic motion, is just affected by the random an frictional terms, so it is no modified. However, when interactions are considered, the diffusion is also affected by hits with the other particles. The external force breaks the isotropy of the system affecting its morphology and thus, the interactions with neighbor particles and, consequently, the diffusion are affected by the external force.

It can be seen in Fig.(4) that the effect of the external force is to increase its diffusion and that the decay of the diffusion with the density is softer for higher forces.

We proceed now to fix the external force to $0.3k_BT\sigma^{-1}$ and introduce fixed particles, which interact through the same interaction potential from Eq.(6). The diffusion coefficient is plotted in front of density for different proportions of fixed particles, $N_{fix}/N_{tot} = 0, 0.5, 0.7, 0.9$, in Fig.(5). Coefficients of variation are between 1% and 8%, being higher for higher proportion of fixed particles.

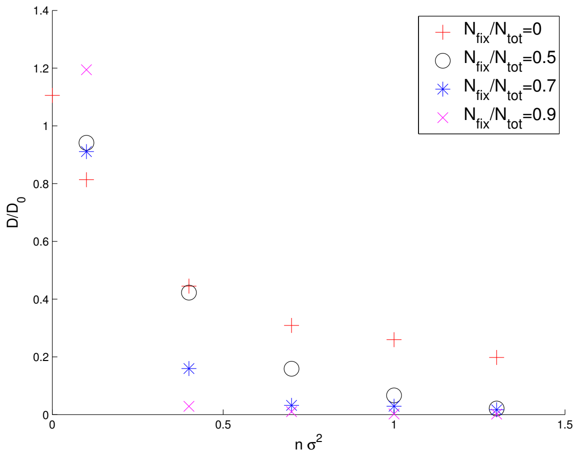

FIG. 5: D/D_0 plotted in front of $n\sigma^2$ for $\sigma f_{ext}/k_BT = 0.3$ proportions of fixed particles $N_{fix}/N_{tot} = 0, 0.5, 0.7, 0.9$. Interaction potential of $U_0 = 10, \lambda = 1$.

It is clear from Fig.(5) that the diffusion coefficient is sensitive to the presence of fixed particles. For $n\sigma^2 = 0.1$, the lowest density, the diffusion coefficient in higher for higher N_{fix}/N_{tot}. However, for higher densities the contrary is observed. Note that a jammed state is reached for all $N_{fix}/N_{tot} > 0.5$, although for higher proportions of fixed particles it happens at lower densities.

This can be understood in terms of two extremal cases. For low densities, the fixed particles exert a force opposite to the driving force, converting part of the drift motion to diffusion, as every time that a moving particle hits a fixed one, it is dispersed. The more obstacles there are, the more frequently dispersed the particles are. Therefore, diffusion increases with N_{fix}/N_{tot}.

On the other hand, for high densities, the space between fixed particles becomes narrower for higher N_{fix}/N_{tot}, hindering the motion until a jammed state is reached. For middle densities, we find the transition from one case to the other.

V. CONCLUSIONS

A study of the diffusion coefficient in a system of Brownian dynamics has been carried out in this paper. It is modeled by Brownian dynamics, in which the particle acceleration is considered to be zero and the hydrodynamic effects neglected. The interaction between particles was modeled by a pairwise Yukawa potential.

The interaction between particles hinders the movement, thus it results in a decay of the diffusion coefficient when the density of particles or the strength of the Yukawa potential are increased. It has been seen that, for stronger interactions, the drop of the diffusion with density is faster and a jammed stated is reached for high densities. In contrast, for weaker potentials the decay is softer and the jammed state is not reached.

Furthermore, the results of two potentials of different characteristic length, one steeper and one softer, are compared with Löwen and Szamel's simulation data, and the diffusions obtained have been very similar, a fast drop of the diffusion for the steeper and a soft decay for the softer, indicating goodness of the results in our simulation.

Additionally, the effect of an external force has been studied, obtaining that it increases the diffusion. In this case, the dependence of the average square displacement per particle with time is not linear but parabolic. When fixed particles are introduced, two opposite effects have been observed. For low densities, an increase of the diffusion due to the dispersion from the fixed particles dominates. On the other hand a jammed state is reached at lower densities when the proportion of fixed particles is higher.

A remaining question is the transition from low densities, where fixed particles favor the diffusion, to high densities, where they block the motion. The jamming process may be described by detailing the flow and spatial correlation functions near the transition point. The results obtained here on the diffusion coefficients could be used as a start point for this future research.

Acknowledgments

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