Separation of Particles by Biased Brownian Motion

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Abstract

In this computer experiment, separation of particles with different sizes, i.e. DNA molecules, was done by a combination of diffusion and a flashing asymmetric periodic potential, a so-called ratchet potential. This method bias the Brownian motion of the particles such that they drift in a preferred direction with a drift velocity that depend on the size of the particle. Hence, this method can, in principle, be used to sort particles with respect to their size. Two regimes were explored: i) the time-independent ratchet potential; and ii) the time-dependent ratchet case, in which a particle is trapped when the potential is turned on and left free to diffuse when the potential is turned off. In both cases, a good agreement with the experimental observations was calculated.

1. Introduction

Particles of different sizes experience different levels of friction and Brownian motion in a solution. By designing an experiment with an appropriately modulated time-dependent and asymmetric electrical field this can be exploited to cause unidirectional motion of particles. If there are two or more species of particles with different size, then the different particles will be separated from each other due to each having its own characteristic drift speed. As an example this could be used for separation of DNA [2].

2. Theory and Numerical Method

Particles in a solution experience random collision with the solvent molecules. The resulting Brownian motion can be described by the Langevin equation [3]. The forces on the particle is split into three components: i) the motion induced by the external potential $U(x,t)$; ii) the viscous drag force that always slows the induced motions down; and iii) a fluctuating force that changes direction and magnitude frequently compared to any other time scale of the system. Then Newton's 2nd Law for a spherical particle of radius r and mass m is:

$$m\frac{\mathrm{d}^2x}{\mathrm{d}t^2} = -\frac{\partial U(x,t)}{\partial x} - \gamma_i\frac{\mathrm{d}x}{\mathrm{d}t} + \xi(t), \tag{1}$$

where $\gamma_i = 6\pi\eta r_i$ is the friction constant, t is the time, x is the position of the particle and the stochastic variable $\xi(t)$ models the random collisions with the other particles in the solution. It is assumed that $\xi(t)$ is an uncorrelated white noise such that $\langle\xi(t)\rangle = 0$ and $\langle\xi(t)\xi(t')\rangle = 2\gamma_i k_B T\delta(t-t')$, where k_B is the Boltzmann constant and T is the temperature of the solution.

In the time scale of interest, the inertial term $m\frac{\mathrm{d}^2x}{\mathrm{d}t^2}$ in Eq. (1) can be neglected since the observation time is much larger than the damping time. Then the equation of interest becomes a first order differential equation in x,

$$\gamma_i\frac{\mathrm{d}x}{\mathrm{d}t} = -\frac{\partial U(x,t)}{\partial x} + \xi(t). \tag{2}$$

To see how diffusion and an external potential can lead to unidirectional motion, consider a flashing potential of the form:

$$U(x,t) = U_r(x)f(t), \tag{3}$$

where $U_r(x)$ is an asymmetric saw-tooth potential of period L given by

$$U_r(x) = \begin{cases} \frac{x}{\alpha L}\Delta U & \text{when } 0 \le x < \alpha L \\ \frac{L-x}{(1-\alpha)L}\Delta U & \text{when } \alpha L \le x < L \end{cases}$$

and $f(t)$ is a square wave signal determining the flashing

of the potential

$$f(t) = \begin{cases} 0 & \text{when } 0 \leq t < \frac{3\tau}{4} \\ 1 & \text{when } \frac{3\tau}{4} \leq t < \tau \end{cases}$$

where $\alpha \in [0, 1]$ is the asymmetry factor and τ is the period of the flashing potential.

This is an asymmetric potential with periodically spaced wells at a distance L apart. The potential flashes on and off in a cyclic manner. If the potential energy is larger than the thermal energy of the particle, the particle will be trapped near the bottom of the well when the potential is on. If there wasn't for Brownian motion, the particle would not move at all even when the potential was off, but because of it, a random walk is added to the situation. While the potential is off, the probability distribution spreads out like a Gaussian function. The density of particles should exhibit diffusion, and after a time t have a distribution like [3]:

$$n(x,t) = \frac{N}{\sqrt{4\pi D t}} e^{-\frac{x^2}{4Dt}}, \tag{4}$$

where N is the total number of particles and $D = k_{\mathrm{B}}T/\gamma_i$ is the diffusion constant.

While the potential is on, the distribution of positions should be consistent with the Boltzmann distribution of occupied potential energy [3]

$$p(U) = \frac{\exp\left(-\frac{U}{k_{\mathrm{B}}T}\right)}{k_{\mathrm{B}}T(1 - \exp\left(-\frac{\Delta U}{k_{\mathrm{B}}T}\right))}. \tag{5}$$

The numerical scheme used in this computer experiment is the forward Euler scheme. This is a method for solving ordinary differential equations with a given initial value. The Euler's method use the concept of local linearity to join multiple small line segments so that they make up an approximation of the actual trajectory. By applying the Euler scheme to Eq. (2), the numerical scheme becomes:

$$x_{n+1} = x_n - \frac{1}{\gamma_i}\frac{\partial U(x_n, t_n)}{\partial x}\delta t + \sqrt{\frac{2k_b T \delta t}{\gamma_i}}\hat{\xi_n}, \tag{6}$$

where δt is the time stip, $t_n = n\delta t$ is the time at the n^{th} step, x_n is the position at the n^{th} step and $\hat{\xi_n}$ is a random number drawn from a centred Gaussian distribution of unit standard deviation.

The Euler scheme is a first-order method. Hence, the local truncation error, the error made per step, will be proportional to the square of the step size $(\delta t)^2$. The Euler method is less accurate than other higher-order techniques for which the local truncation error is proportional to a higher power of the step size. The global truncation error, the error at a fixed time t, is the cumulative effect of the local truncation errors committed at each step. This can be approximated by the number of steps $((t - t_0)/\delta t \propto 1/\delta t)$ times the error committed at each step $(\propto (\delta t)^2)$. Thus, the global truncation error will be approximately proportional to the step size.

Rounding errors will be introduced since the numerical precision of the computer is limited. The machine epsilon ϵ is the maximum relative error due to rounding in floating point arithmetic. In other words, ϵ is difference between one and the smallest float larger than one. After N steps the combined rounding error will be approximately $N\epsilon y_0$ if it is assumed that the rounding errors in each step n is about the same size, $\epsilon y_n \sim \epsilon y_0$. If all rounding error point in the same direction, the total rounding error will be $\propto \epsilon/\delta t$, since $N \propto 1/\delta t$.

The time step should not be so large that a single step could make the particle jump through several potential wells. The increment in position should, with a large probability, occur in a region of constant force. Since the shortest interval of constant force is of length αL, the increment in position should satisfy $|x_{n+1} - x_n| \ll \alpha L$. By making a upper-bound of $|x_{n+1} - x_n|$ from Eq. (6) and using that the probability of having $\hat{\xi} < 4$ is greater than 99.99%, the time criterion becomes:

$$\frac{1}{\gamma_i}\max\left|\frac{\partial U}{\partial x}\right|\delta t + 4\sqrt{\frac{2k_{\mathrm{B}}T\delta t}{\gamma_i}} \ll \alpha L. \tag{7}$$

Before starting on the numerical method, we introduce the following reduced units:

$$\hat{x} = \frac{x}{L},$$
$$\hat{t} = \omega_i t,$$
$$\hat{U}(\hat{x}, \hat{t}) = \frac{U(x,t)}{\Delta U},$$

where $\omega_i = \Delta U/(\gamma_i L^2)$. Eq. (6) then becomes

$$L\hat{x}_{n+1} = L\hat{x}_n - \frac{\Delta U}{L\omega_i\gamma_i}\frac{\partial\hat{U}(\hat{x}_n,\hat{t}_n)}{\partial\hat{x}}\delta\hat{t} + \sqrt{2\frac{k_bT\delta}{\omega_i\gamma_i}\hat{t}}\,\hat{\xi}_n$$

Introducing $\hat{D} = k_BT/\Delta U$ this becomes:

$$\hat{x}_{n+1} = \hat{x}_n\frac{\partial\hat{U}(\hat{x}_n,\hat{t}_n)}{\partial\hat{x}}\delta\hat{t} + \sqrt{2\hat{D}\delta\hat{t}}\,\hat{\xi}_n. \tag{8}$$

In reduced units, the time constraint in Eq. (7) becomes

$$\max\left|\frac{\partial\hat{U}}{\partial\hat{x}}\right|\delta\hat{t} + 4\sqrt{2\hat{D}\delta\hat{t}} \ll \alpha, \tag{9}$$

and the flashing potential in Eq. (3) becomes

$$\hat{U}(\hat{x},\hat{t}) = \hat{U}_r\hat{f}(\hat{t}), \tag{10}$$

where the asymmetric saw-tooth potential now is given by

$$\hat{U}_r(\hat{x}) = \begin{cases} \frac{\hat{x}}{\alpha} & \text{when } 0 \le x < \alpha \\ \frac{1-\hat{x}}{(1-\alpha)} & \text{when } \alpha \le x < 1 \end{cases} \tag{11}$$

and the flashing function now is given by

$$\hat{f}(\hat{t}) = \begin{cases} 0 & \text{when } 0 \le \hat{t} < \frac{3\omega_i\tau}{4} \\ 1 & \text{when } \frac{3\omega_i\tau}{4} \le \hat{t} < \omega_i\tau. \end{cases} \tag{12}$$

```
! Gaussian distributed random numbers
function random_gauss() result(↩
    rand_gauss)
    real(wp), intent(out) :: ↩
        rand_gauss
    real(wp)              :: rand1, ↩
        rand2, w = 0._wp
    integer               :: i

    do while(w == 0._wp .OR. w >= 1)
        call random_number(rand1)
        call random_number(rand2)
        rand1 = rand1 * 2._wp - 1._wp
        rand2 = rand2 * 2._wp - 1._wp
        w = rand1**2 + rand2**2
    end do
    rand_gauss = rand1 * SQRT( - 2._wp↩
        * LOG(w) / w)
end function
```

Figure 1: Implementation of the Box-Müller algorithm in the programming language Fortran.

2.1. The Gaussian Distributed Random Number Generator

A Gaussian probability distribution is used to model the particles Brownian motion. The stochastic variable ξ is obtained using the Box-Müller algorithm. The implementation in Fortran can be seen in figure 1. When plotting the theoretical Gaussian distribution with mean zero and unit standard deviation together with the distribution of a million numbers drawn with the algorithm, see figure 2, they have a strong resemblance.

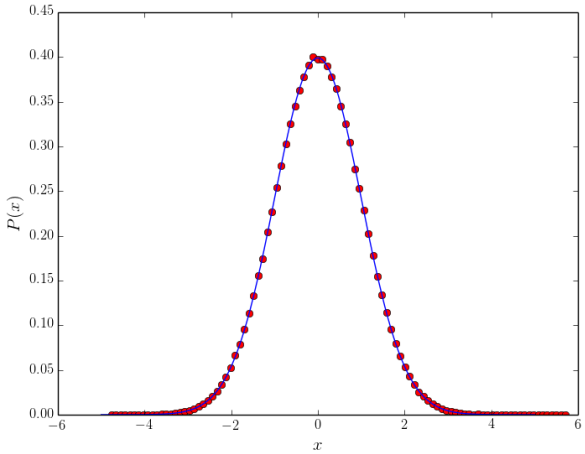
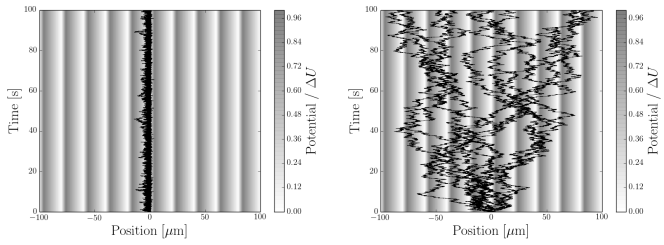


Figure 2: Plot of the theoretical Gaussian normal distribution with mean zero and unit standard deviation (blue line) together with the distribution of a million numbers drawn with the Box-Müller algorithm (red circles).

3. Results and discussion

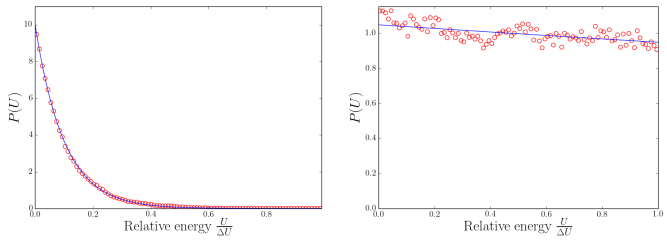
If the strength of the ratchet potential is much smaller than the thermal energy k_BT of the particle, the effect from the potential on the particle will be negligible [1], see figure 3b. Hence, ΔU have to be larger than the thermal energy of the particle so that the particle will get trapped when the potential is turned on, see figure 3a. The amplitude ΔU was taken to be 80 eV so that the particle has time to reach the bottom of the well while the potential is still on. The distribution of positions is consistent with the Boltzmann distribution of Eq. (5) as one should expect according to statistical mechanics, see figure 4.

When the potential is turned off, the particle diffuses symmetrically to a new position. The particle density of an



(a) $\Delta U = 10 k_\mathrm{B} T$. **(b)** $\Delta U = 0.1 k_\mathrm{B} T$.

Figure 3: Typical trajectories of particles in a non-flashing ratchet potential showed with two different potential strengths ΔU for 10 particles.



(a) $\Delta U = 10 k_\mathrm{B} T$. **(b)** $\Delta U = 0.1 k_\mathrm{B} T$.

Figure 4: The experimental distribution of occupied potential energy plotted with the Boltzmann distribution with two different potential strengths ΔU.

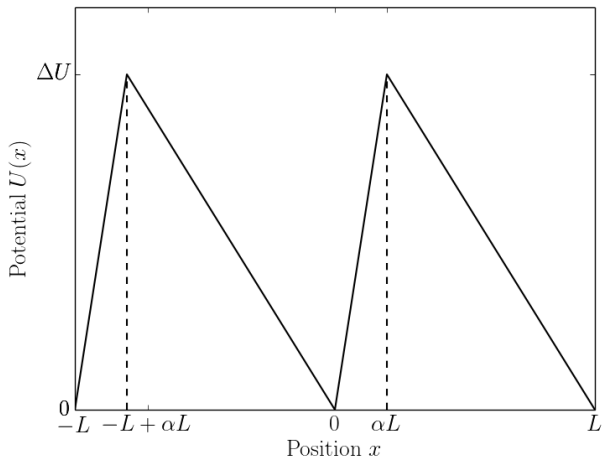


Figure 5: The potential $U(x)$ is an asymmetric sawtooth function with asymmetry factor α. The amplitude is ΔU, and the wells (potential minima) are spaced periodically with a distance L apart.

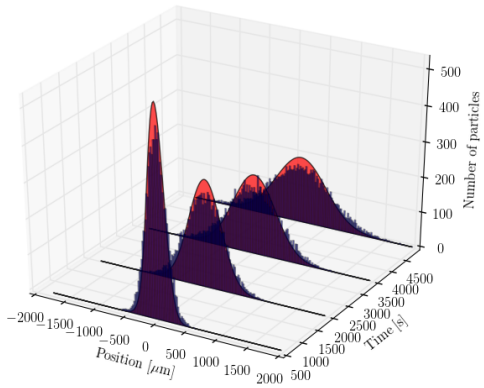


Figure 6: The motion of an ensemble of particles which are not impacted by a potential plotted with $n(x, t)$ from Eq. (4)

ensemble of particles will diffuse out and follow the distribution of Eq. (4), see figure 6. When the potential is turned on again, the particle will get trapped in the well spanning its new position. Because of the asymmetry of the potential, see figure 5, a particle is more likely to feel a force to the right ($P(\text{right}) = 1 - \alpha$) than to the left ($P(\text{left}) = \alpha$). And hence, the particle will be more likely to be trapped in a well to the right of the starting position than in a well to the left of the starting position when the potential is turned on. And thus, a net motion to the right occurs.

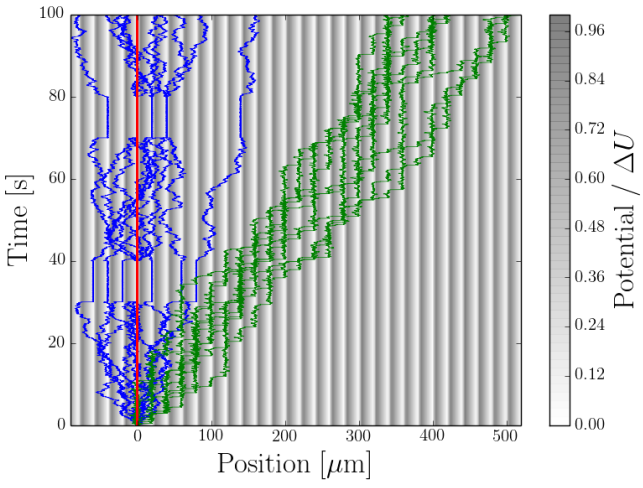


Figure 7: Typical trajectories in a flashing ratchet potential showed for different periods τ of the flashing. High frequency flashing ratchet with $\tau = 0.01$ (red line). Medium frequency flashing ratchet with $\tau = 0.5$ (green line). Low frequency flashing ratchet with $\tau = 40.0$ (blue line).

The drift velocity v_d of the particle depends on the frequency of the flashing. The three regimes of drift efficiency with respect to the flashing period τ is the following, see figure 7: i) τ is so small that a particle is not able to diffuse the short distance αL, and hence, do not have time to diffuse to the neighbouring potential well to the right before the potential is turned on again; ii) τ is so large that a particle is able to diffuse the longer distance $(1-\alpha)L$, and hence, have time to diffuse both to the left and right potential well before the potential is turned on again; and iii) τ is so that a particle is able to diffuse at least the distance αL, but not longer than the distance $(1-\alpha)L$ while the potential is off, and hence, just have time to diffuse over to the nearest neighbouring potential well to the right before the potential is turned on again.

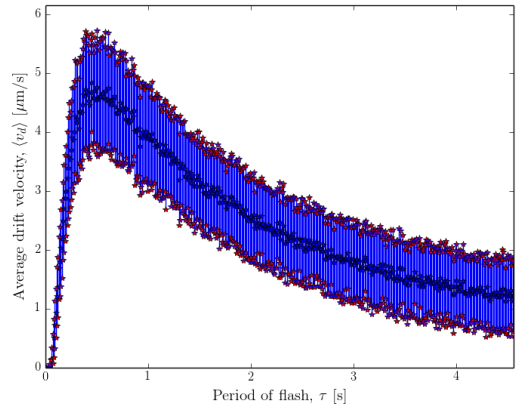
In the following experiments, ΔU is set to 80 eV as mentioned above. When computing the average drift velocity v_d as a function of the flashing period τ, the optimal flashing period τ_op can be found as the one that maximises the drift velocity, see figure 8. When the radius of the particle is 12 nm, τ_op is approximately 0.44 s with a maximum drift velocity of about $(4.9 \pm 0.3)\,\mu\mathrm{ms}^{-1}$.

The only place where the radius r appear in the Euler scheme given by Eq. (8), is in the expression for the time step in reduced units:

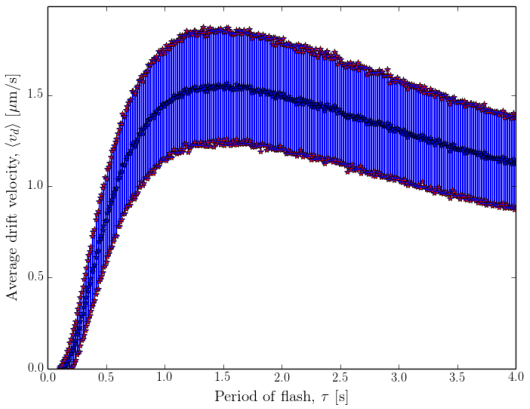
$$\delta\hat{t} = \frac{\Delta U}{6\pi\eta r L^2}\delta t.$$

This means that if r is doubled then $\delta\hat{t}$ is halved. Hence, this is equivalent to a change of time scale. Thus, one would expect that for a particle with a radius of 36 nm the drift velocity with respect to flashing period would have a similar shape as that for the particle with a radius of 12 nm, but have a three times longer period and a drift velocity of a third for the same point on the curve, see figure 8b. When the radius of the particle is 36 nm, τ_op is approximately 1.42 s with a maximum drift velocity of about $(1.5 \pm 0.1)\,\mu\mathrm{ms}^{-1}$.

By tuning τ so that the drift velocity is maximised for a particular particle specie, separation of particles by size may be achieved. By running the system for two different kind of particles, for example one type with three times as large radius, and setting the flashing period to be the optimal for the smaller particle, then the smaller particle



(a) Particle with radius $r = 12$ nm.



(b) Particle with radius $r = 36$ nm.

Figure 8: Average drift velocities for two different sized spherical particles for different temporal periods τ. The drift velocity is induced by cyclically turning an anisotropic sawtooth potential ($\alpha = 0.2$) on and off ($t_\mathrm{on} : t_\mathrm{off} = 3{:}1$). The spatial period of the potential was $L = 20\,\mu$m. The coefficient of viscous drag was $\gamma_i = 6\pi\zeta r_i \approx 2.3 \cdot 10^{-10}\,\mathrm{Nsm}^{-1}$ where $\zeta = 1 \cdot 10^{-3}\,\mathrm{Pa\,s}$.

will move much faster to the right while the larger will stay behind, see figure 9.

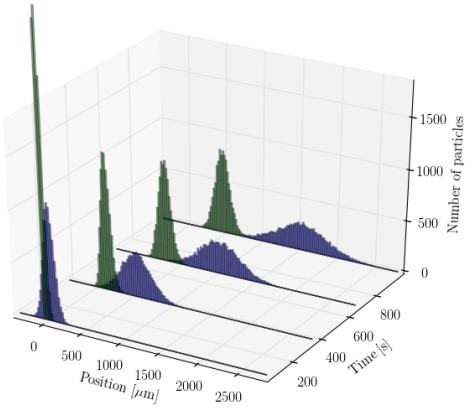


Figure 9: The motion of two ensembles of particles, with radius of 12 nm and 26 nm respectively, in a flashing ratchet potential.

The behaviour observed is a combination of two processes: diffusion and advection. Therefore the advection diffusion equation would be able to describe the particles density behaviour. The advection diffusion equation in one dimension is the following

$$\frac{\partial f}{\partial t} + v\frac{\partial f}{\partial x} = D\frac{\partial^2 f}{\partial x^2}.$$

The amplitude ΔU was taken to be 80 eV. Such a large ΔU is necessary for the approximations inherent in this simple picture given to be fulfilled. An exact calculation using the diffusion equation would probably result in qualitatively the same behaviour for smaller values of ΔU as well.

4. Conclusion

It has been observed that by tuning the flashing period of a ratchet potential it is possible to separate particles by size. This method bias the Brownian motion of the particles such that they drift in a preferred direction with a drift velocity that depend on the size of the particle. E.g. if having two different particle types, where one is twice as big as the other, it is possible to get the smaller one to diffuse away from the larger one by tuning the flashing period of the potential. The observed numerical behaviour is in good agreement with theoretical equations.

5. References

[1] R. D. Astumian. Thermodynamics and kinetics of brownian motor. *Science 9*, 256(5314):917–922, 1997.

[2] J. S. Bader, R. W. Hammond, S. A. Henck, M. W. Deem, G. A. McDermott, J. M. Bustillo, J. W. Simpson, G. T. Mulhern, and J. M. Rothberg. DNA transport by a micromachined brownian ratchet device. *Proceedings of the National Academy of Sciences of the United States of America*, 96(23):13165—-13169, November 1999.

[3] J. P. Banon. *Computational Physics (TFY4235/FY8904): Assignment 1 - Biased Brownian Motion: An Application to Particle Separation.* Norwegian University of Science and Technology, 2016.