Dynamics of two coupled particles: comparison of Lennard-Jones and spring forces

Renata Retkute[a] and James P. Gleeson[a]

[a]Department of Applied Mathematics, UCC, Cork, Ireland;

ABSTRACT

The motion of elastically coupled Brownian particles in ratchet-like potentials has attracted much recent interest due to its application to transport processes in many fields, including models of DNA polymers. We consider the influence of the type of interacting force on the transport of two particles in a one-dimensional flashing ratchet. Our aim is to examine whether the common assumption of elastic coupling captures the important features of ratchet transport when the inter-particle forces are more complex. We compare Lennard-Jones type interaction to the classical case of elastically coupled particles. Numerical simulations agree with analytical formulas for the limiting cases where the coupling is very weak or very strong. Parameter values where the Lennard-Jones force is not well approximated by a linearization of the force about the equilibrium distance are identified.

Keywords: Brownian ratchet, Langevin equation, collective behaviour, Lennard-Jones potential.

1. INTRODUCTION

The motion of Brownian particles in ratchet-like potentials[1] has attracted great interest due to its wide applications in connection with transport processes in many fields including nanotechnologies.[2] Experiments have demonstrated the possibility of particle transport in a ratchet-like potential generated by applying a voltage difference to interdigitated electrodes.[3,4] The traps periodically vanish and the particles undergo Brownian motion after the electrodes are discharged. When applying an ac electric field, because of the difference in the electrophoretic mobilities it is possible to observe directional motion with shorter clusters moving faster then longer ones. This allows the separation of polymers with different lengths.

Directed motion of particles in ratchet devices has been studied recently by many workers. For a single particle, thermal noise and an asymmetric potential produce motion of the particle in a direction that depends on the asymmetry of the potential.[5] It is desirable, however, to study more complex systems than single particles. Several authors have studied the motion of two coupled particles in "flashing ratchets",[6–8] where the switching of the potential is governed by various stochastic or time-periodic processes. A net current in the presence of thermal noise occurs due to the fact that the slopes of the sawtooth potential of the ratchet are different in the forward and backward directions. The potential is switched on and off in time; in the case of alternating periodic dichotomous process for each particle,[6] directional motion can be induced even in the absence of thermal fluctuations due to the compressibility of the spring and the independent switching of the potentials. In this regime the current decreases monotonically with increasing intensity of noise. For the case of strong coupling and switching governed by multiplicative nonwhite fluctuations,[7] the current shows dependence on the correlation time of fluctuations and on the equilibrium distance between particles. The interaction between the particles clearly influences the directed motion — an effective potential for the center-of-mass of particles has been proposed[8] in order to understand this behaviour.

However, the models of interacting particles considered so far are based on spring-type coupling. In this work, we concentrate on the connection between the directed transport and the type of interaction force between the pair of particles. As an alternative to the spring model, we introduce a Lennard-Jones interaction between particles. The initial motivation to study this model emerges from the possibility of applying ratchet mechanisms in the sorting of DNA fragments by size using electric fields. The Lennard-Jones potential works reasonably well for electrically neutral, polarizable, spherical molecules. Although complex molecules such as polymer chains

Further author information: (Send correspondence to R. Retkute)
R. Retkute : E-mail: rr1@cs.email.lt, Telephone: 353 21490 4204

require complicated potentials to describe the interaction between monomers, we believe that the present study is the first step towards a more realistic model.

The paper is organised as follows. In the next section we present the Brownian ratchet model for single particle and two interacting particles, together with both coupling models. In Sec. 3 we elaborate on the theoretical calculations for limiting cases where both models show similar results. Numerical results for a set of parameters values identifying regimes where both models show qualitatively different currents are shown, and conclusions are drawn in Sec. 4.

2. MODEL FOR SINGLE AND INTERACTING PARTICLES

Before discussing transport of two coupled particles, we identify optimal values for the flashing ratchet parameters for a single particle. A pointlike overdamped particle is placed in a periodic, asymmetric potential which is periodically switched on and off[5]:

$$\gamma \frac{dx}{dt} = -z(t)\partial_x W(x) + \sqrt{2D}\xi(t), \tag{1}$$

where γ is a constant friction coefficient, x the position of the particle, $W(x)$ the ratchet potential it experiences, D is the diffusion coefficient, and $\xi(t)$ denotes white noise with zero mean and correlation given by $\langle \xi(t)\xi(s) \rangle = \delta(t-s)$. The time dependence of the ratchet, $z(t)$, is a periodic dichotomous process taking the values 0 and 1:

$$z(t) = \begin{cases} 0, & 0 \le t < \tau/2, \\ 1, & \tau/2 \le t < \tau. \end{cases} \tag{2}$$

We consider a piecewise linear but asymmetric ratchet potential $W(x)$ of periodicity L:

$$W(x) = \begin{cases} \frac{A}{\alpha} x, & 0 \le x < \alpha L, \\ \frac{A}{(L-\alpha)}(L-x), & \alpha L < x \le L, \end{cases} \tag{3}$$

where A is the height of barrier and α is parameter of asymmetry. If $\alpha < \frac{1}{2}$ the transport is in positive direction, and in the negative direction otherwise. We will use the following values of parameters if not stated otherwise: $\gamma = 1$, $\alpha = 0.1$, $L = 1$ and $A = 1$.

The statistical properties of the driven stochastic process $x(t)$ are described in terms of an ensemble of realizations. The main quantity of interest here is the net current of particles, defined by

$$j = \lim_{T\to\infty} \frac{\langle x(T) - x(0) \rangle}{T}.$$

The Langevin equations (1)-(3), are solved by employing the second order Runge-Kutta method[9] for stochastic differential equations (SDE) with a time step of $\Delta t = 10^{-3}$. All quantities of interest are averaged over 200 different realizations, each single trajectory consisting of 10^6 integration steps.

In Figure 1 we investigate the dependance of current on two parameters defining ratchet and random fluctuations: the period of ratchet switching, τ, and the intensity of noise, D. Our calculations indicate the existence of an effective noise intensity which maximizes current. If the intensity of noise is too small, then the particle cannot overcome the ratchet maximum during the on phase of the potential. On the other hand, if noise intensity is too high, the probability of particle moving to the left of the initial position is equal to probability of particle moving to the right, giving zero current on average. The results also show that the current is sensitive to the switching period τ, with a nonmonotonic dependence on τ for low and high intensities of noise. For moderate intensity of noise D (in the range from 0.02 to 0.2) the current first decreases with τ, and then increases. A slight shift in the value of D corresponding to maximum current is observed as τ changes. The insert in Figure 1 shows current as a function of the asymmetry parameter α for noise intensities $D = 0.1$ and $D = 0.01$. As α increases from 0.1 to 0.5, the current decreases and is equal to 0 at $\alpha = 1/2$. For the case $D = 0.1$ the dependence of current on asymmetry coefficient can be approximated by the line $j = -0.5(\alpha - 0.5)$ and for case $D = 0.01$ by the line $j = -0.01(\alpha - 0.5)$.

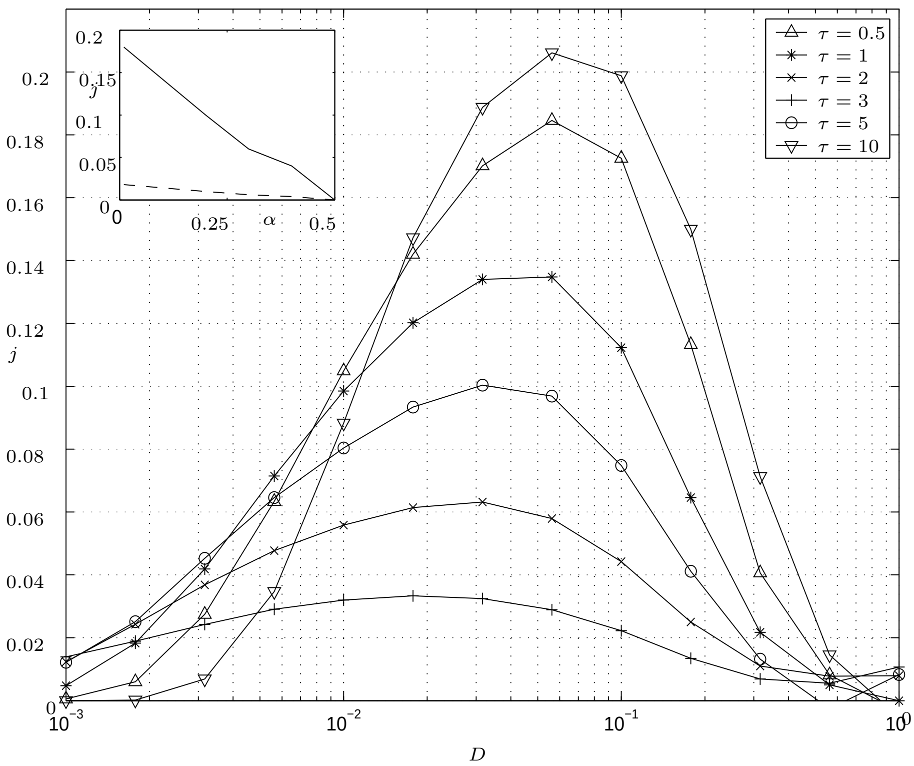

Figure 1. The average current of single particle as a function of the noise intensity for different values of switching period. Insert: the average current as a function of asymmetry coefficient for different values of noise intensity: 0.01 (solid line) and 0.1 (dashed line).

Elastically coupled particles have been discussed previously in the literature, but most models consider particles subject to an additional external force as well as to the ratchet.[10] We are interested in the case where particles interact only with each other and with the flashing potential in the presence of thermal noise, i.e. no external "rocking" force is used.

The equations of motion of two interacting, overdamped particles are:

$$\gamma \dot{x_1} = -z(t)\frac{\partial W(x_1)}{\partial x_1} - \frac{\partial U}{\partial x_1} + \sqrt{2D}\xi_1, \tag{4}$$

$$\gamma \dot{x_2} = -z(t)\frac{\partial W(x_2)}{\partial x_2} - \frac{\partial U}{\partial x_2} + \sqrt{2D}\xi_2, \tag{5}$$

where $x_1(t)$ and $x_2(t)$ are the positions of the particles, and $\xi_i(t)$ denotes white noise with zero mean and correlation given by $\langle \xi_i(t)\xi_j(s)\rangle = \delta(t-s)\delta_{ij}$. The ratchet potential $W(x)$ is as described in equation (3), and the interaction potential $U(x_1, x_2)$ describes the coupling between the particles.

The potential function for elastic spring interaction takes the form:

$$U_{SP}(x_1, x_2) = \frac{k(x_2 - x_1 - a)^2}{2}. \tag{6}$$

where k and a are the spring constant and equilibrium distance, respectively. The Langevin equations (4)-(6), are solved by the same second order Runge-Kutta method[9] as described above. The current j is now defined as the average velocity of the mid-point of the two particles, defined by

$$j = \lim_{T\to\infty} \frac{\langle x_{MP}(T) - x_{MP}(0)\rangle}{T}, \tag{7}$$

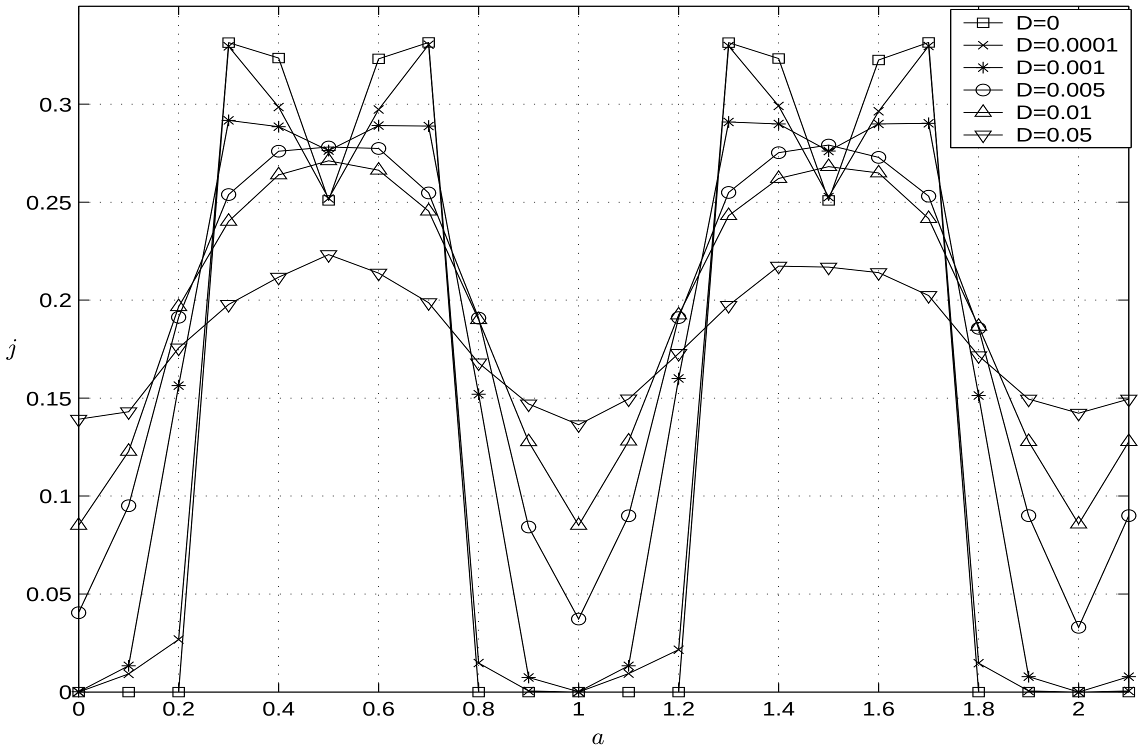

Figure 2. The average current of two elastically coupled particle as a function of the equilibrium distance for different values of noise intensity. Here $k = 2$ and $\tau = 1$.

where x_{MP} is the coordinate of the mid-point of the pair of particles.

An important feature of the spring-coupled model is that, for certain parameter values, transport of particles can occur even when no random fluctuations are present. The condition on the parameters[11]

$$nL + 2\alpha L < a < nL + L - 2\alpha L, \tag{8}$$

(where n is an integer) means that this noiseless current can appear for a wide variety of values of equilibrium length a. This mode of motion arises when the spring is stretched and compressed during 'on' and 'off' phases of the ratchet. If the equilibrium length of the spring is larger then the short section of the sawtooth potential, one particle can be pushed or pulled to a neighboring minimum of the potential, see reference 11 for details.

In Figure 2 we have plotted the transition of the current from the case of no random forcing, $D = 0$, to fluctuations of high intensity, $D = 0.05$. It could be observed that for specific set of parameters, $k = 2$ and $\tau = 1$, nonzero transport appears for equilibrium distance a in the range from $0.2 + i$ to $0.8 + i$, i=0,1,2... Calculations indicate that the current is periodic in a with period equal to the period L of the ratchet device. For the case where fluctuations are present, transport of particles is present for all a values, although the maximum in the current curve corresponds to the maximum of the deterministic case.

In order to investigate the effects of more realistic interaction between particles, we compare the classical spring model to a Lennard-Jones (LJ) interaction. The Lennard–Jones force between two molecules is given by the potential function[12]:

$$U_{LJ}(r) = 4\epsilon\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right), \tag{9}$$

where ϵ is the strength of interaction and the distance between particles is $r = |x_2 - x_1|$. We choose the value of parameter σ such that the minimum of Lennard-Jones potential is at the spring equilibrium distance, i.e.

$\sigma = a \cdot 2^{-1/6}$. The Lennard-Jones potential is mildly attractive as the two particles approach one another from a distance, but strongly repulsive when they approach too close. At equilibrium, the pair of particles reach a separation corresponding to the minimum of the Lennard–Jones potential.

A somewhat similar situation was studied in references 13 and 14, where the particles were assumed to be hard rods and the interaction between two particles was approximated with a hard core repulsion. The average velocity dependence on the particle size was shown to be a discontinuous function in the limit where the average distance between the two particles goes to zero. In this paper we focus on investigating whether the usual elastic coupling assumption can accurately model more complicated potentials such as Lennard-Jones.

3. RESULTS AND DISCUSSION

We are interested in comparing the effect of Lennard-Jones interaction with the classical spring model. If we assume that the distance between the particles $|x_2 - x_1|$ is close to the equilibrium length of the spring or LJ force, we can Taylor-expand the potential (9) around a and find the effective value of the spring constant, $k = k_{eff}$, in terms of the LJ parameters:

$$k_{eff} = \frac{72\epsilon}{a^2}. \tag{10}$$

3.1. Similarities in the models

Numerical simulation indicate that for the limits of weak coupling, $k \to 0$, and for rigid coupling, $k \to \infty$, elastic coupling and interaction via Lennard-Jones potential gave the same values of net current. We use a simple approximation[15] to estimate the current in the $k = 0$ case of independent particles, which reduces to the single particle model of Sec. 2. In the $k \to \infty$ limit the particles again move as a single particle, but in a different effective potential. We show here that the approximation method can be used to estimate the current in this case.

Consider a single particle subject to a ratchet potential with height U sufficiently large (compared to D) that hopping over barrier is very improbable. If the period τ of the flashing is sufficiently large, then the probability distribution of the particle position when potential is on can be assumed to consist of delta functions at the minima of the potential. When the potential is turned off, each of the spikes will start to diffuse. The delta spike at $x = 0$, for instance, spreads during the diffusive period of time τ according to a Probability Distribution Function (PDF)[15]:

$$P(x) = \frac{1}{\sqrt{4\pi D\tau}} e^{-\frac{x^2}{4D\tau}}. \tag{11}$$

The probability to diffuse to the left of initial minimum is thus given by the complementary error function:

$$j_L = \int_{-\infty}^{(1-\alpha)L} P(x)dx = \frac{1}{2} Erfc\Big(\frac{(1-\alpha)L}{2\sqrt{D\tau}}\Big). \tag{12}$$

Similarly, the probability of motion to the right is

$$j_R = \int_{\alpha L}^{\infty} P(x)dx = \frac{1}{2} Erfc\Big(\frac{\alpha}{2\sqrt{D\tau}}\Big). \tag{13}$$

When travelling left or right, each particle cover a distance L to the next spike location, from where it can diffuse again later after time 2τ. If we consider the case $\alpha < 1/2$ the current to the right is given approximately by

$$J = \frac{L}{2\tau}(j_R - j_L) = \frac{L}{2\tau}\frac{1}{2}\Big(Erf\Big(\frac{(1-\alpha)L}{2\sqrt{D\tau}}\Big) - Erf\Big(\frac{\alpha L}{2\sqrt{D\tau}}\Big)\Big). \tag{14}$$

The case of rigidly coupled particles is essentially equivalent to the single particle case subject to a modified potential. Using the idea of the effective potential for the center-of-mass of particles,[8] we can find modified parameters to use formula (14) for the current. For $a = 0.5 + n, n = 1, 2...$ we have found that effective period is $\tilde{L} = L/2$ and effective noise level is $\tilde{D} = D/2$.[16]

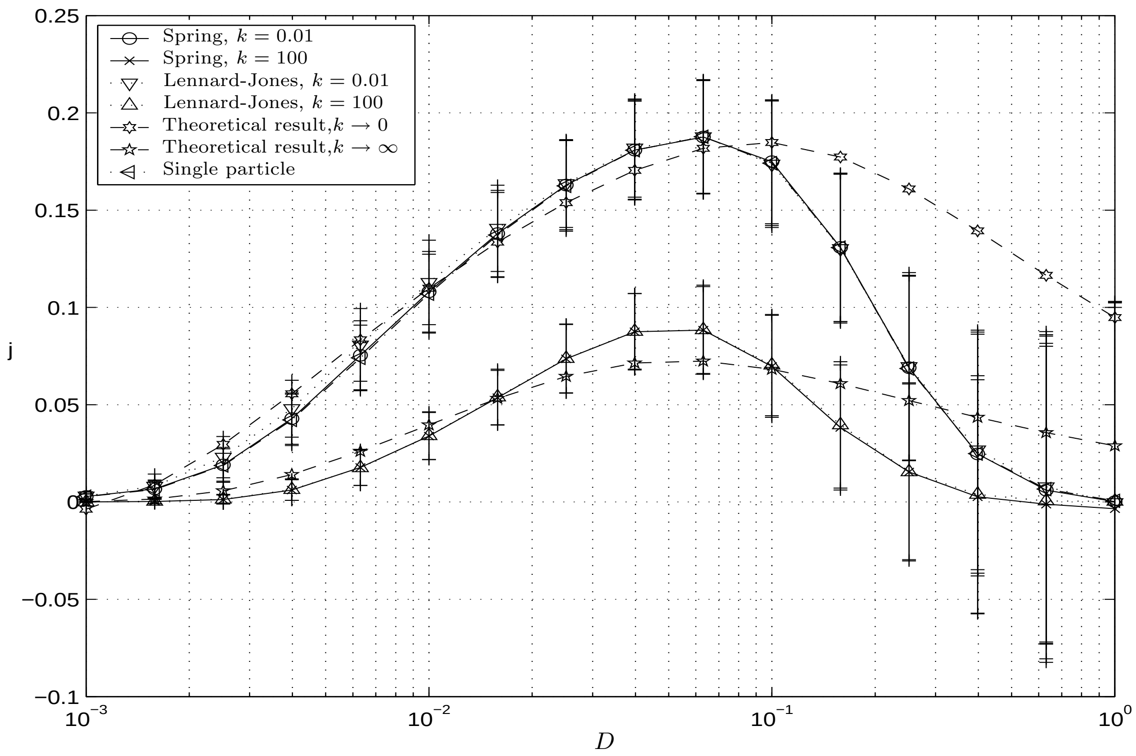

Figure 3. The average current as a function of noise intensity, numerical simulations (solid lines) and theoretical result (dashed lines) for $\tau = 1$.

Figure 3 shows a comparison between the theoretical formula (14) and numerical simulations for single particle and coupled particles for limiting cases $k = 10^{-2}$ and $k = 10^{2}$. Numerical results indicate that spring coupling and coupling via LJ potential gave very similar results. In the limit $k = 0.01$ these also agreed with results for single particle driven under the same values of parameters. Using simulation results we can identify the limits where formula (14) successfully approximates both models. The results of the theoretical formula and numerical simulations agree quite well for small values of noise intensity: $D < 10^{-1}$.

3.2. Differences in the models

We have found that the difference between the Lennard-Jones and spring coupling models is observable for small a values and k values in the range from 10^{-1} to 10^{1}. For a fixed value of k, the spring model shows a periodic response as a function of a, but the Lennard-Jones model lacks periodicity for small values of a.

Figures 4 - 7 show the average current of two particle coupled via spring and Lennard-Jones potentials as a function of the (effective) spring constant for different values of equilibrium distance, with noise intensity $D = 0.01$ (Figure 4), $D = 0.05$ (Figure 5), $D = 0.1$ (Figure 6) and $D = 0.2$ (Figure 7). Due to the periodicity, spring coupling produces the same current for equilibrium distances satisfying condition $a + Ln$, $n = 0, 1, 2....$ All figures clearly illustrate how the LJ coupling approaches the spring coupling when the equilibrium distance is increased by the ratchet period $L = 1$.

As has been discussed in the previous section, in the limit of weak coupling $k \to 0$, both models approach the case of two single particles and so give similar results. We calculated the following values of net current for any equilibrium distance and the coupling $k = 0.01$: $j = 0.12$ for $D = 0.01$, $j = 0.21$ for $D = 0.05$, $j = 0.18$ for $D = 0.1$ and $j = 0.12$ for $D = 0.2$. It should be mentioned that the current does not depend on the value of equilibrium distance for weak coupling between particles.

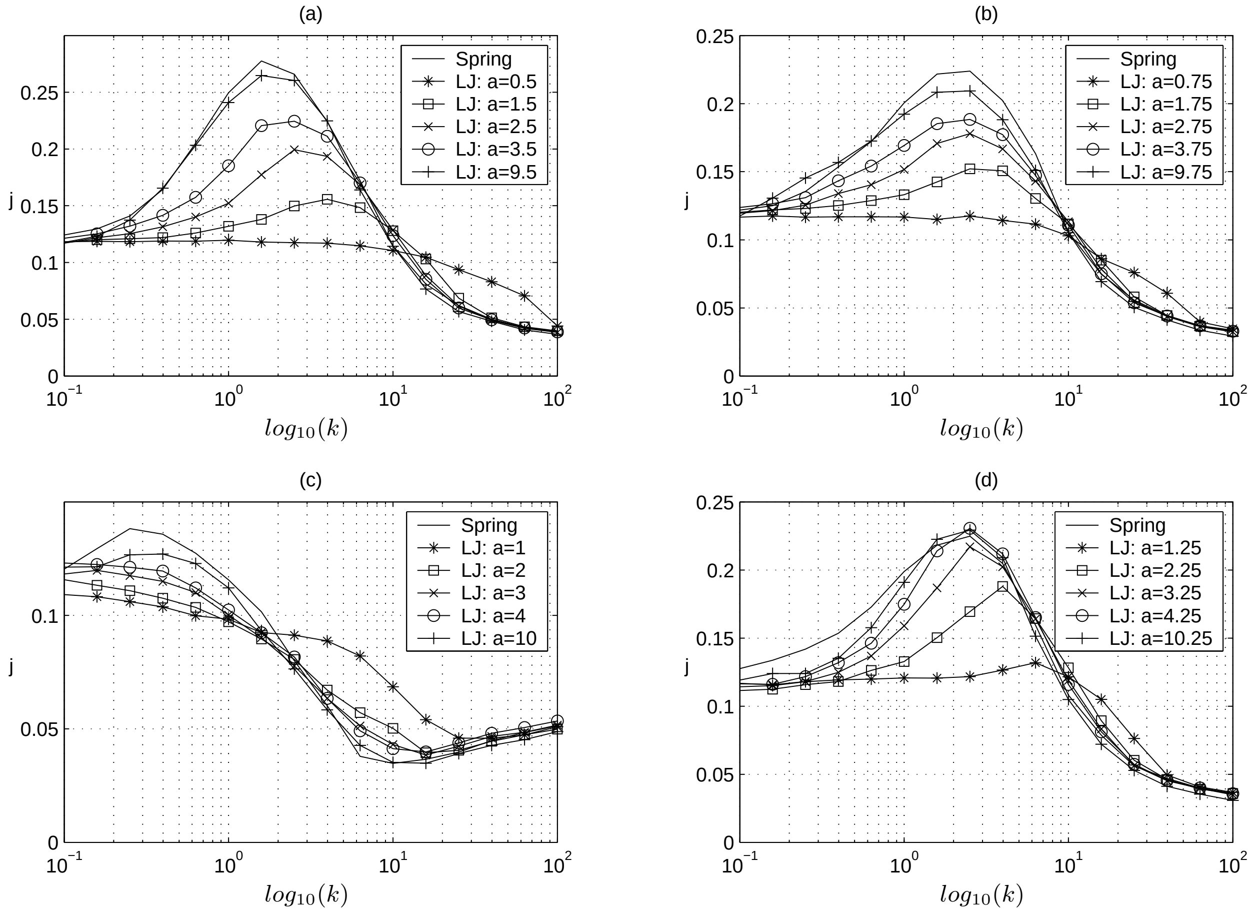

Figure 4. The average current of two particle coupled via spring and Lennard-Jones potentials as a function of the spring constant for different values of equilibrium distance for $D = 0.01$.

In the case of strong coupling, i.e. $k \to \infty$, the particles are rigidly coupled to each other. Our numerical simulations indicate that the actual threshold for k to observe this type of behaviour depends on the value of noise strength D: asymptotic behaviour requires larger values of k as the intensity of noise increases. For larger noise intensities, introducing stronger coupling between the particles causes the current to decrease until the spring and LJ the currents both reach the $k \to \infty$ limit. It also can be observed that the current value in the rigid limit has a strong dependance on the equilibrium distance, which can be explained by an effective potential model.[16]

Details of the results for moderate coupling are rather complex and show strong dependency on the value of D as well as periodicity in a. This can be explained by the fact that harmonically coupled particles are able to move directionally in the absence of thermal noise (see equation (8) above), while transport in the LJ model requires nonzero noise intensity for small values of a.

For small noise $D = 0.01$ (Figure 4) and for any values of a for spring coupling and $a > 1$ for LJ coupling, our simulations show that the current has a maximum in the range of k from 10^{-1} to 10^{1}. For any fixed value of a, two regimes of current can be identified. If parameters satisfy formula (8), the maximum current $j = 0.24$ is observed near $k = 1$. In the second regime, maximum current $j = 0.14$ is at $k = 0.1$ and minimum current $j = 0.04$ is at $k = 100$.

Parts (a) to (d) of Figures 4 to 7 correspond to different fractional parts of the equilibrium length a. The behaviour of the current depends strongly on the fractional part of a, especially for lower noise levels D, as the

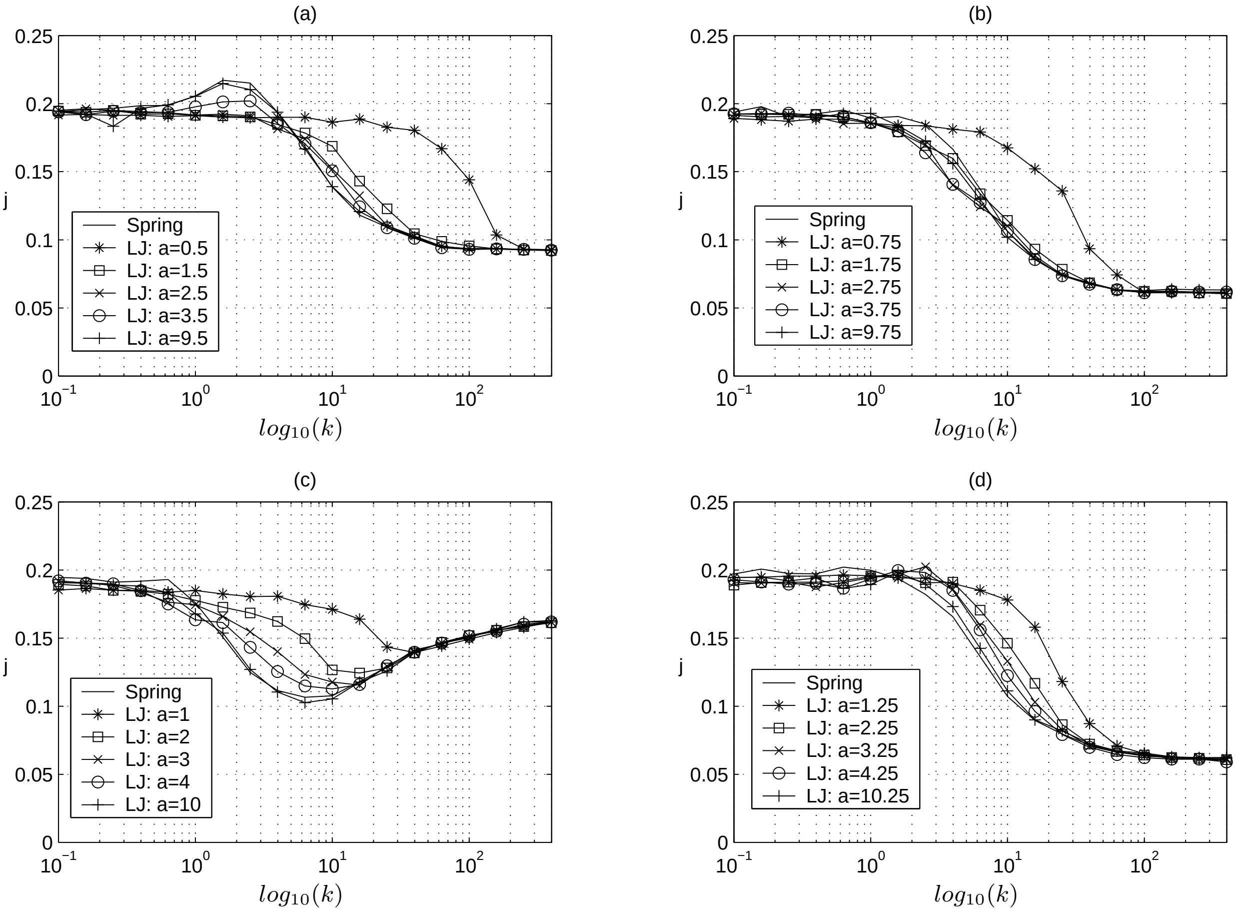

Figure 5. The average current of two particle coupled via spring and Lennard-Jones potentials as a function of the spring constant for different values of equilibrium distance for $D = 0.05$.

noiseless current predicted by inequality (8) can then dominate. As the intensity of noise is increased, the current becomes less dependent on condition (8).

Some understanding of the differences between the two coupling models may be obtained using the approach of Wang and Bao,[8] who examined elastically coupled pairs of particles. They show that when the noise intensity D is sufficiently low and the coupling k is sufficiently strong, the distance between the particles $y = x_1 - x_2$ has a Gaussian distribution of mean a and standard deviation $\sqrt{D/k}$. This prediction is verified by our numerical simulations (not shown), though we note it applies only to the case where noiseless transport is absent, i.e. when (8) is not satisfied. Since the linearization of the LJ potential about $y = a$ gives the effective spring coupling (10), we expect that if $y(t)$ remains confined near a then LJ and spring effects will coincide. Thus we have a simple condition: if $\sqrt{D/k} \ll a$, then the LJ coupling current is indistinguishable from the equivalent spring coupling case. We note that the case of noiseless transport obeying (8) requires further refinement of this rule-of-thumb.

4. CONCLUSIONS

In the present work, we have explored the influence of the type of interacting force on the transport of two coupled particles moving in a one-dimensional flashing ratchet. Our main objective has been to identify the parameter regimes where LJ interaction produces qualitatively different results compared to elastic coupling.

We have discussed how current depends on the strength of thermal noise D, equilibrium distance a, and strength of interaction k. Regimes where both LJ and spring models show similar behaviour have been identified:

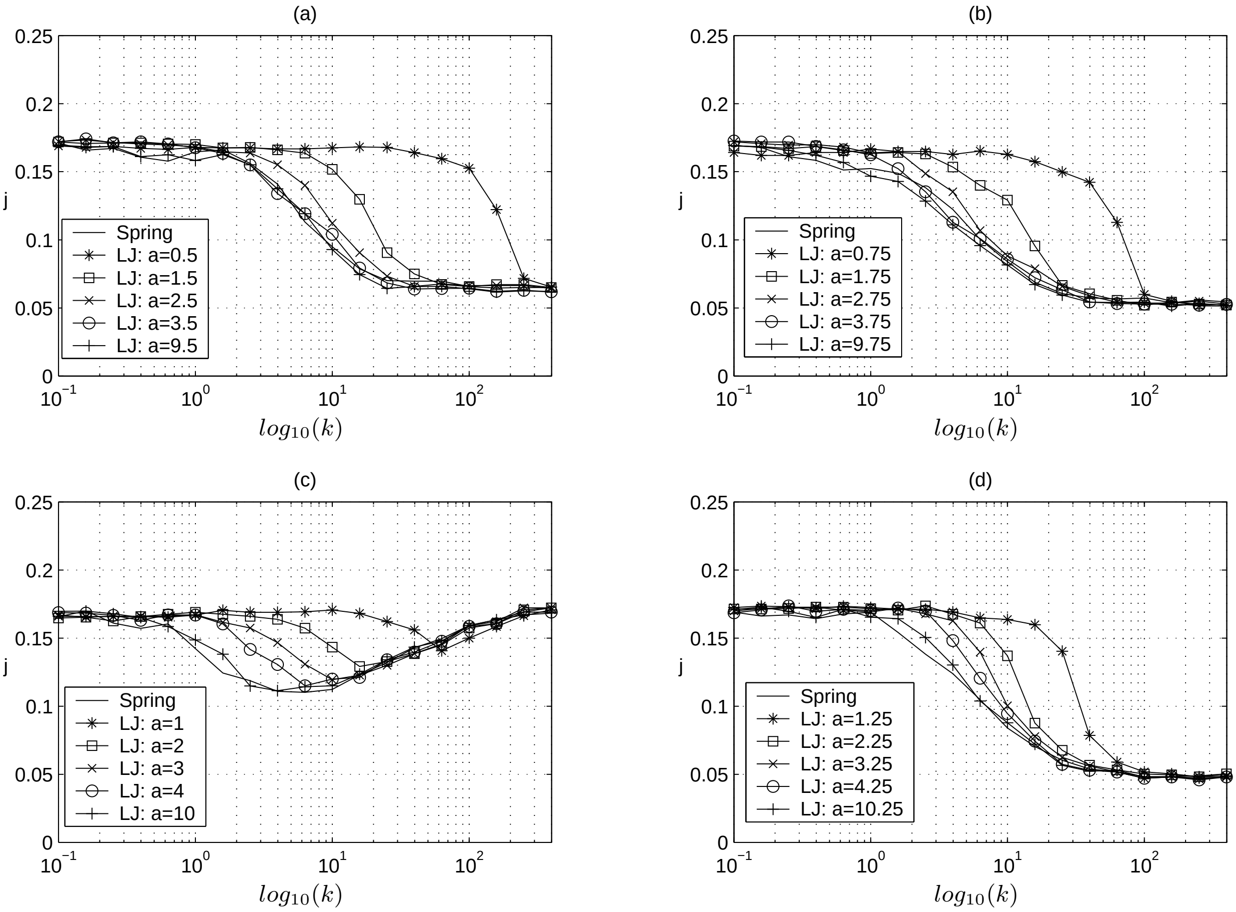

Figure 6. The average current of two particle coupled via spring and Lennard-Jones potentials as a function of the spring constant for different values of equilibrium distance for $D = 0.1$.

(a) for weak coupling $k \to 0$, (b) strong coupling $k \to \infty$ and (c) large equilibrium distance a. Details of the results for moderate coupling are rather complex and show strong dependency on the value of D.

Our results from exploring a subset of parameter space indicate that the Lennard-Jones interaction can have important effects upon the current which are not captured by linearizing the force to a spring model. Further refinement of the model, for example increasing the number of interacting particles, is clearly necessary to describe polymer chains more realistically.

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REFERENCES

1. M. Magnasco, "Forced thermal ratchets," *Phys. Rev. Lett.* **71**, pp. 1477–1481, 1993.
2. G. Slater, S. Guillouzic, M. Gauthier, J. Mercier, M. Kenward, L. McCormick, and F. Tessier, "Theory of DNA electrophoresis (similar to 1999-2002(1)/(2))," *Electrophoresis* **23**, pp. 3791–3816, 2002.
3. J. S. Bader, R. W. Hammond, and S. A. Henck, "DNA transport by a micromachined brownian ratchet device," *PNAS* **96**, pp. 13165 – 13169, 1999.
4. R. Hammond, J. Bader, S. Henck, M. Deem, G. McDermott, J. Bustillo, and J. M. Rothberg, "Differential transport of DNA by a rectified Brownian motion device," *Electrophoresis* **21**, pp. 74–80, 2000.

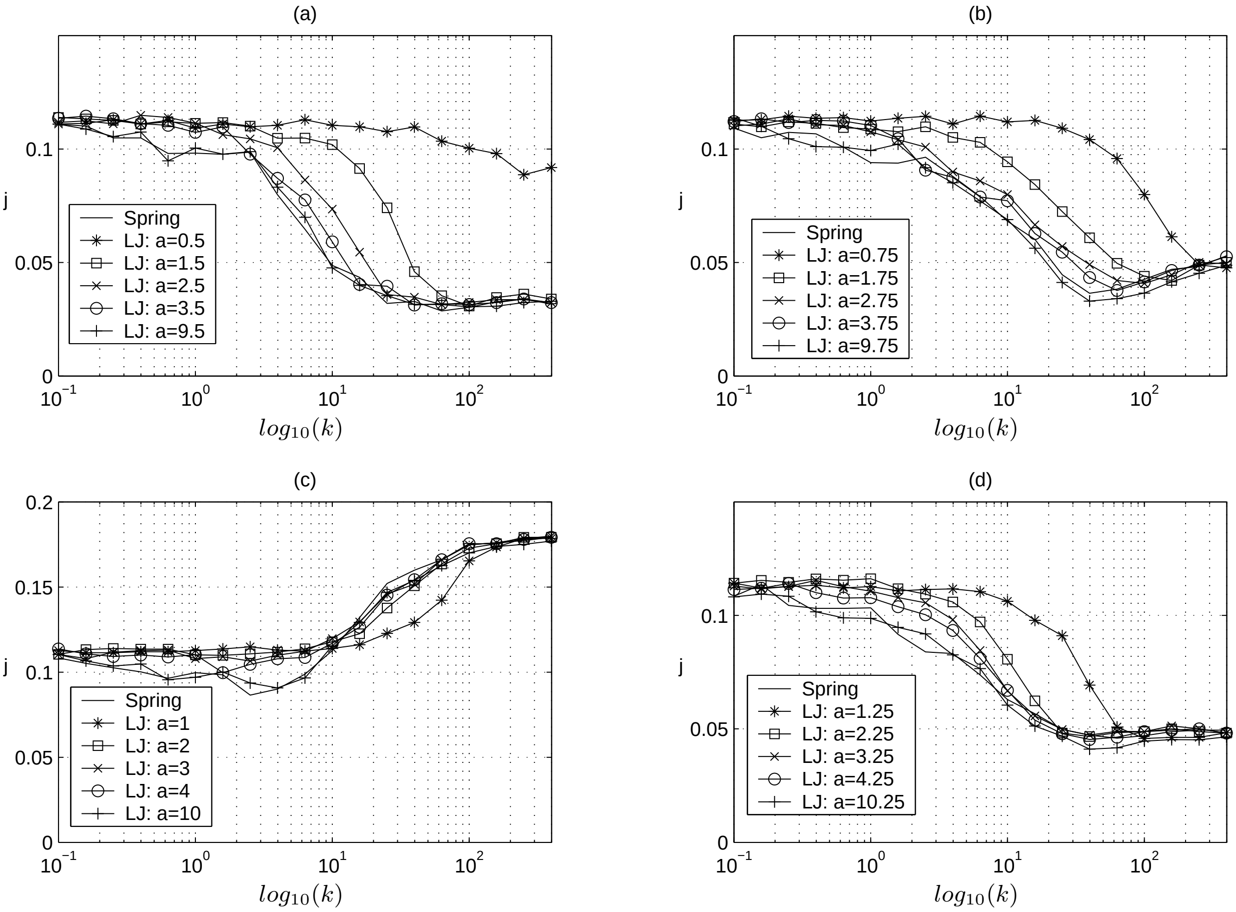

Figure 7. The average current of two particle coupled via spring and Lennard-Jones potentials as a function of the spring constant for different values of equilibrium distance for $D = 0.2$.

5. M. Magnasco, "Forced thermal ratchets," *Phys. Rev. Lett.* **71**, pp. 1477–1480, 1993.
6. D. Dan, A. Jayannavar, and G. Menon, "A biologically inspired ratchet model of two coupled Brownian motors," *Physica A* **318**, pp. 1477–1480, 2003.
7. S. Klumpp, A. Mielke, and C. Wald, "Noise-induced transport of two coupled particles," *Phys. Rev. E* **63**, pp. 031914–031920, 2001.
8. H. Wang and J. Bao, "The roles of ratchet in transport of two coupled particles," *Physica A* **337**, pp. 13–26, 2004.
9. P. Kloeden and E. Platen, *Numerical solution of stochastic differential equations*, Springer-Verlagy, Paris, 1992.
10. P. Reimann and P. Hanggi, "Introduction to the physics of Brownian motors," *App. Phys. A* **75**, pp. 169–178, 2002.
11. A. Ajdari, "Force-free motion in an asymmetric environment - a simple-model for structured objects," *J. Phys. I France* **4**, pp. 1577–1582, 1994.
12. D. Ceperley, M. Kalos, and J. Lebowitz, "Computer-simulation of dynamics of a single polymer-chain," *Phys. Rev. Lett.* **41**, pp. 313–316, 1978.
13. I. Derenyi and T. Viscek, "Cooperative transport of Brownian particles," *Phys. Rev. Lett.* **75**, pp. 374–377, 1995.
14. I. Derenyi, P. Tegzes, and T. Viscek, "Collective transport in locally asymmetric periodic structures," *Chaos* **9**, pp. 657–664, 1998.

15. R. Astumian and M. Bier, "Fluctuation driven ratchets - molecular motors," *Phys. Rev. Lett.* **72**, pp. 1766–1769, 1994.
16. R.Retkute and J. Gleeson, "Effect of the Lennard-Jones interaction on noise-induced transport of two coupled particles," in preparation.