

PAPER: Classical statistical mechanics, equilibrium and non-equilibrium

# Diffusion of chains in a periodic potential

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Received 17 May 2017

Accepted for publication 17 July 2017

Published 18 September 2017



Online at [stacks.iop.org/JSTAT/2017/093204](http://stacks.iop.org/JSTAT/2017/093204)  
<https://doi.org/10.1088/1742-5468/aa82be>

**Abstract.** We studied the diffusion of 1D rigid chains in a square wave potential of period  $T$ . We considered chains of type A (composed of  $N$  particles A) and chains of type A–B (composed of  $N/2$  particles A and  $N/2$  particles B). The square wave potential represents domains, a lamellar structure observed for block copolymers, in which the repulsive  $\delta$  energy between each A particle (B particle) of the chain and B particles (A particles) of the medium where the chains diffuse. From Monte Carlo simulations and analytical results it is found that the normalized diffusivity  $D$ , for  $N \ll T$ , presents a universal behavior as a function of  $X = N\delta$  for chains of type A and  $X = (N\delta - \ln T^2)$  for chains of type A–B, with and exponential decay for large values of  $X$ . For fixed values of  $\delta$  and  $T$ ,  $D$  is a periodic function of  $N$  with period  $T$  and  $2T$  for chains of type A and type A–B, respectively.

**Keywords:** diffusion

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**1. Introduction**

Diffusion of a homopolymer chain in a melt is a very complex process. Since chains cannot cross each other, they become topologically entangled leading to a type of diffusion known as reptation [1–6]. The local dynamics of block copolymer segments is similar to those of pure homopolymers. However, block copolymers present a phase separation due to repulsion between dissimilar blocks that affects the dynamics on a length scale larger than the size of the domains. A well ordered block copolymer does not change its shape for a long time even when the temperature is above its glass transition temperature, but segments of the blocks can move freely within the domains having a liquid character [7–10].

For block copolymers, the presence of domains significantly reduces the diffusion in the direction perpendicular to the interface between the domains. In this direction, block copolymer chains diffuse through an activated hopping mechanism in which blocks must overpass regions energetically unfavorable. Consequently, diffusion coefficients of block copolymers decrease exponentially with the activation energy of the hopping process that directly depends on the chain length [11–17].

Motivated by the above problem, in the present work we introduce a simple model (probably the simplest possible model) to study the diffusion of a chain in a periodic potential. This periodic potential resembles the interaction energy of a polymeric chain with a diblock copolymer forming a lamellar structure. The main objective is to study the behavior of this model from a theoretical point of view, even when some conclusions could be extended to real systems.

## 2. The chain model

Firstly let us consider the diffusion of a single particle A in a 1D lattice with a periodic potential of period  $T$ , see figure 1(a). In a discrete version of diffusion, the jumping rates between nearest neighbor lattice sites, separated by a distance  $a = 1$ , are shown in figure 1(b). The origin of the periodic potential could be due to a lamellar structure having particles A in region I and particles B in region II. The energy  $\delta$  corresponds to the repulsive interaction between the diffusive particle A and the substrate in region II composed of particles B. In region I the interaction between particle A and substrate is considered to be zero (that is,  $\delta$  is the difference of the energies of the particle A when it is located in region II and in region I). In this article we use dimensionless energies in terms of  $k_B T_0$ , where  $k_B$  is the Boltzmann constant and  $T_0$  the absolute temperature.

Secondly we consider the diffusion of a rigid chain composed of  $N$  particles A in the same periodic potential of figure 1(a). In the following this chain will be called as chain A. The total energy of a chain A, as a function of position of the chain center  $x_c$ , is shown in figure 1(c) for  $N < T/2$ .

Similarly, for a single particle B that diffuses on the same substrate, the interaction in region I is  $\delta$  and zero in region II (see figure 2(a)). Then, we consider the diffusion of a rigid chain composed of  $N/2$  particles A (half left) and  $N/2$  particles B (half right) in the same substrate. In the following this chain will be called as chain A–B. The total energy for chains of type A–B, as a function of position of the center of the chain  $x_c$ , is shown in figure 2(b) for  $N < T/2$ .

The main objective of the present work is to obtain the behavior of the diffusion of both types of chains as a function of the length  $N$  for a given period  $T$  of the potential.

For a chain of length  $N$  the jumping rate (for a jump to the right or to the left of distance  $a$ ) is given by

$$\begin{aligned} k &= (k_0/N)\exp[-(E_f - E_i)], & \text{if } E_f > E_i \\ k &= (k_0/N), & \text{if } E_f \leq E_i \end{aligned} \quad (1)$$

where  $E_f$  and  $E_i$  are the energy of the chain in the final and initial position of the center of the chain, respectively ( $|E_f - E_i| = \delta$  or 0, see figures 1(c) and 2(b)). For a chain of type A diffusing in a homogeneous substrate (that is  $\delta = 0$ , and then regions I and II are equivalent, see figure 1(a)] the diffusion coefficient  $D_0$  is

$$D_0 = k_0 a^2 / N, \quad (2)$$

where the term  $1/N$  take into account the usual decrease of the diffusivity with the length of the chain. In order to take into account the influence of the periodicity of the potential energy we will compute the normalized diffusivity  $D = D_c / D_0$ , where  $D_c$  is the diffusion coefficient of the center of the chain with the jumping rate of equation (1), and  $D_0$  is given by equation (2).

We use standard Monte Carlo simulations. At each Monte Carlo step the chain jumps, to the right or to the left, with the jumping rate of equation (1) and the time,  $t$ , is increased by 1. The repetition of this procedure simulates the random motion of the chain in a lamellar structure. The simulation starts with a chain in an arbitrary lattice site and finishes after the chain moves several periods of distance along the lattice. The

Monte Carlo results of  $D_c$ , were obtained averaging over more than  $10^3$  samples, and is calculated through

$$D_c = (\Delta^2 x_c) / 2t, \quad (3)$$

where  $\Delta^2 x_c = [x_c(t) - x_c(0)]^2$ ,  $x_c$  is the position of the center of the chain, and the brackets denote the ensemble average.

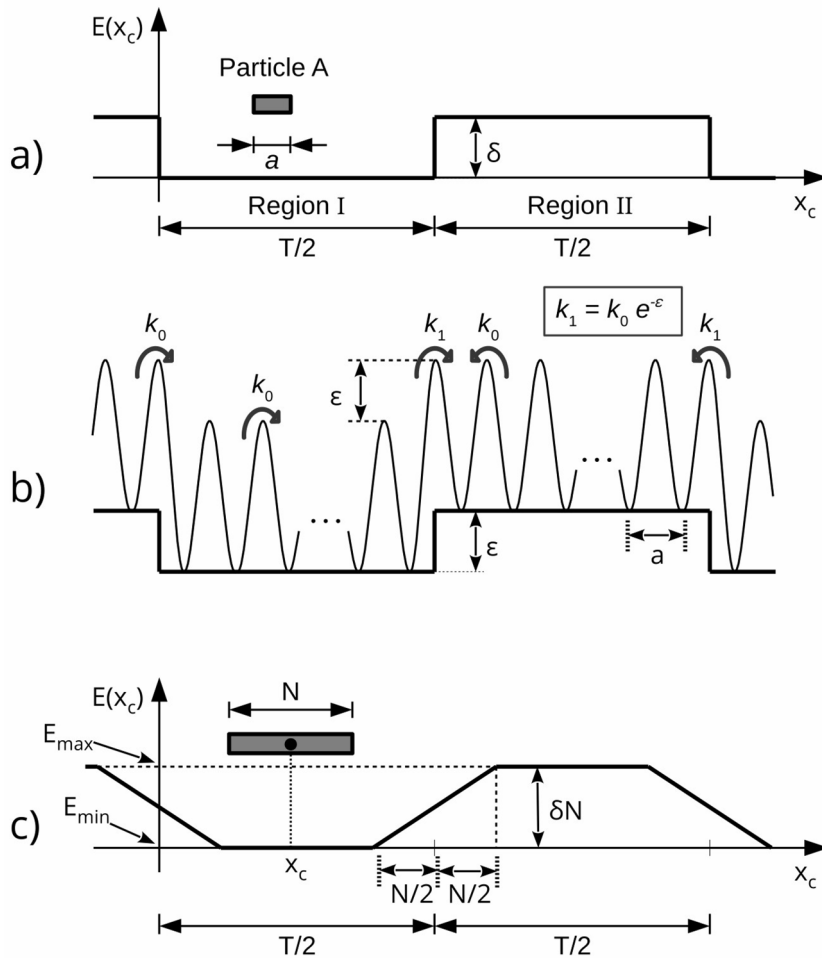
### 3. Results

Due to the periodicity of the potential energy, one expects a periodicity in the normalized diffusion coefficient of the chain  $D$  as a function of  $N$ . It is easy to note that a chain of type A of length  $N = nT$ , where  $n$  is any integer greater than zero, the energy difference  $E_f - E_i$  is equal to zero, independently of the position  $x_c$ , and then  $D = 1$ . From a more general analysis one finds that  $D$  is a periodic function with period  $T$ . Using similar arguments, one can deduce that for chains of type A–B, the normalized diffusion coefficient  $D$  versus  $N$  is a periodic function with period  $2T$ .

Numerical results of  $D$  against  $N$  for chains of type A–B are shown in figure 3 for two different values of  $T$ . It is easy to see that the normalized diffusivity presents a local maximum around  $N = 2T$  with  $D = 1$ . Other numerical results (with different  $\delta$  and  $T$ , and for chains of type A), not included in this work, present the same behavior. This is in agreement with the arguments presented above. Thus, we conclude that  $D$  as a function of  $T$  is a periodic function of  $N$  for chains of type A and chains of type A–B.

In figure 4, the behavior of the normalized diffusion coefficient of the chain for chains of type A–B as a function of  $N$ , for different values of  $\delta$ , is shown. The inset of figure 4 clearly indicates that the relevant parameter to study the behavior of  $D$ , for small values of  $N$ , is the energy  $E = N\delta$ . From the numerical results obtained for chains of type A (not shown here) we arrive to the same conclusion. In the following, we will focus on the behavior of  $D$  against  $E$ , when  $D$  is far from its first minimum value, i. e., for  $N \ll T/2$  and  $N \ll T$  for chains of type A and A–B respectively (see figure 3). The free parameters of the systems are  $T$  and  $E$ . The value of  $N$  for which  $D$  shows a minimum is due to the gap,  $\Delta E = N\delta$ , between the maximum,  $E_{\max}$ , and minimum,  $E_{\min}$ , of the total energy of the chain that presents a maximum for  $N = T/2$  and  $N = T$  for chains of type A and A–B respectively (see figures 1(c) and 2(b)).

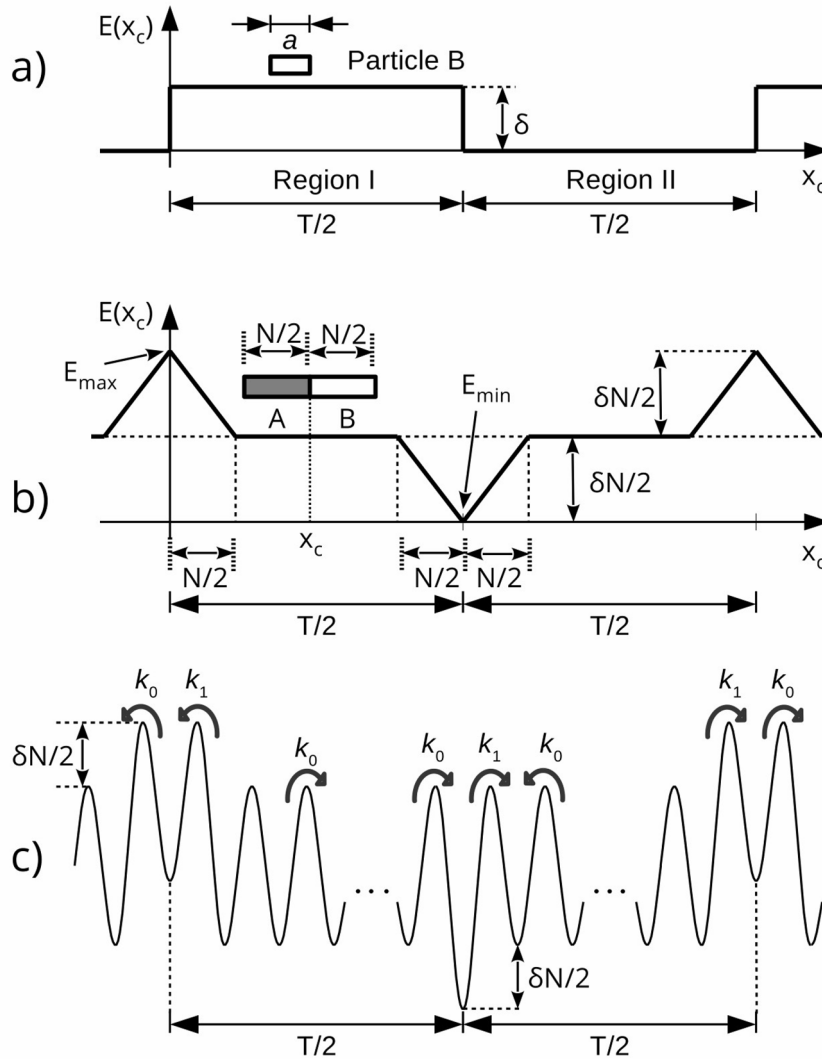
Figures 5 and 6 show the numerical results of  $D$  versus  $N$ , for different values of the period  $T$ , in semi-logarithmic scales, for chains A and A–B, respectively. Note that in both cases, after an initial plateau,  $D$  exhibits an exponential decay. Interestingly, for chains A results do not depend on  $T$ . For chains A–B and large values of  $E$ ,  $D$  behaves as  $T^2 \exp(-E)$ . To verify the dependence on  $T$  in the inset of figure 6 we plot  $\ln D$  versus  $(E - \ln T^2)$ , for different values of  $T$ . The data collapse obtained clearly confirm the dependence on  $T^2$ , and shows that, for large enough values of  $T$ ,  $D$  can be expressed as a scaling function of  $X = (E - \ln T^2)$ , with  $D = 1$  for small values of  $X$ , and  $D \propto \exp(-X)$  for large values of  $X$ . Note in figures 5 and 6 that the exponential decay is valid as  $D$  changes orders of magnitude.



**Figure 1.** Periodic potential (a) and jumping rates (b) for a single particle A that diffuses in a lamellar structure (periodic potential).  $k_0$  and  $k_1$  (where  $\varepsilon = \delta$ ) are the jumping frequencies, between nearest neighbor lattice sites separated by a distance  $a$ . In (c), total energy of a rigid chain composed of  $N$  particles of type A, as a function of position of the center of the chain  $x_c$ , for  $N < T/2$ . The maximum,  $E_{\max}$ , and minimum,  $E_{\min}$ , of the total energy of the chain are indicated with arrows. The rigid chain diffuses in the same lamellar medium that (a) and (b). For the point model A the jumping rates also are indicated in (b), but now  $\varepsilon = \delta N$ . Note that this substrate resembles the energy landscapes for chains of types A shown in (c), for  $N \ll T/2$ .

#### 4. The particle model

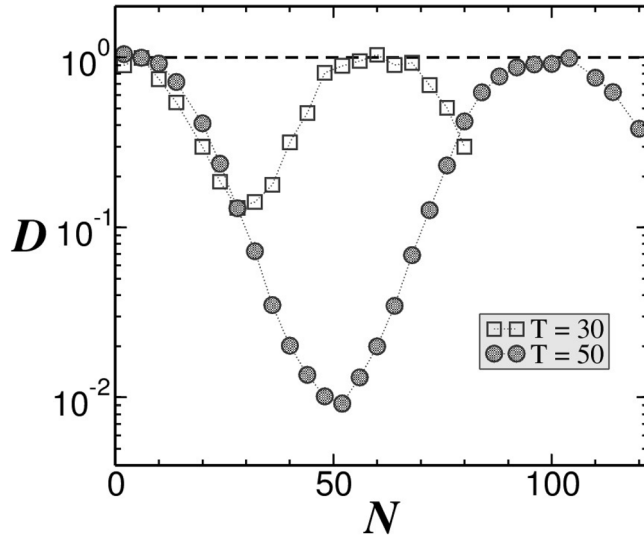
In order to obtain analytical results, we simplify the chain models not taking into account the finite length of the chains. Firstly let us consider chains of type A. Then, in the simplified version, chains are considered as point particles diffusing in the substrates shown in figure 1(b) with the energy  $\varepsilon = \delta N$ . This substrate resembles the energy landscapes for chains of types A shown in figure 1(c), for  $N$  much smaller than  $T/2$ . In other words, the size of the original chain is only taken into account through the energy  $\varepsilon$  in the simplified model of chain A, which we will denote as point model A.



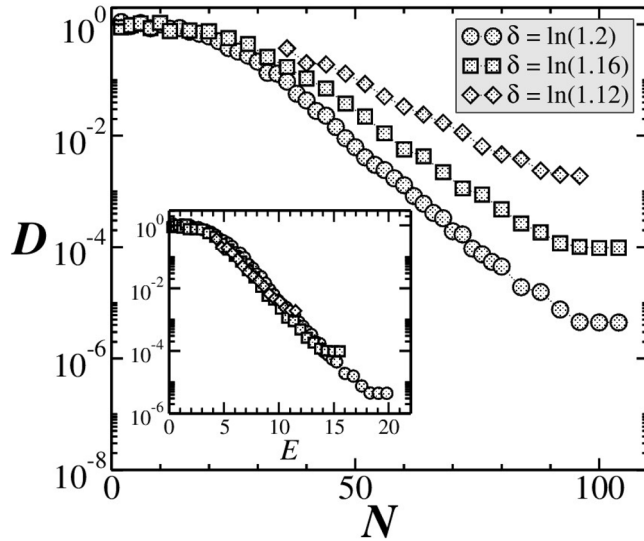
**Figure 2.** (a) Periodic potential for a single particle B in the same lamellar medium as figure 1. In (b), total energy of a rigid chain composed by  $N/2$  particles A (half left) and  $N/2$  particles B (half right), as a function of position of the center of the chain  $x_c$ , when  $N < T/2$ . The maximum,  $E_{\max}$ , and minimum,  $E_{\min}$ , of the total energy of the chain are indicated with arrows. The rigid chain diffuses in the same lamellar medium as (a). In (c), jumping rates for a single particle of the point model A–B that diffuses in a periodic arrangement of energetic barriers where  $k_1 = k_0 \exp(-\delta N/2)$  which resemble the energy landscapes for chains of types A–B shown in (b), for  $N \ll T$ .

Let us now consider chains of type A–B. In the simplified version the point particle diffuses in the substrate shown in figure 2(c), that resemble the energy landscapes for chains of types A–B shown in figure 2(b), for  $N$  much smaller than  $T$ . This simplified version we will denote as point model A–B.

Despite the crude approximations used, the behavior of the normalized diffusion constant  $D$  for the simplified models reproduces the general tendencies of  $D$  for the corresponding chain models. More specifically, for point model A one can obtain that  $D$  is given by (see appendix)



**Figure 3.** Normalized diffusivity,  $D$  against  $N$ , of rigid chains of type A–B for two different periods of the potential energy. Monte Carlo results were obtained averaging over 2000 samples with  $\delta = 0.18$ . Note that  $D$  is a periodic function of period  $2T$ .

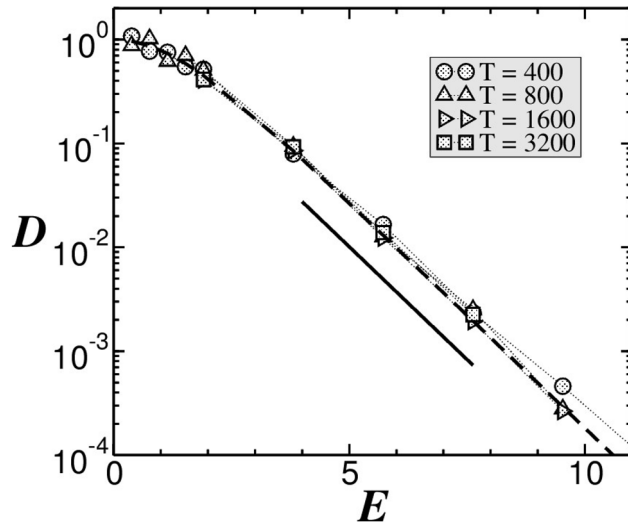


**Figure 4.** Main graph: normalized diffusivity,  $D$ , of rigid chains of type A–B versus  $N$  for different values of  $\delta$  with  $T = 100$ . Inset: the same values of normalized diffusivity against energy,  $E$ , ( $E = N\delta$ ). Monte Carlo results were obtained averaging over 1000 samples.

$$D = \frac{2T}{T + \left(\frac{T}{2} + 1\right) \exp(E) + \left(\frac{T}{2} - 1\right) \exp(-E)}. \tag{4}$$

Interestingly,  $D$  practically does not depend on  $T$  and rapidly adopts an exponential dependence with  $E$  (see caption of figure 5). Indeed, for large values of  $E$  and  $T$ , it can easily be shown that  $D$  decreases as  $4\exp(-E)$ , independently of  $T$ . This tendency is in





**Figure 5.** Normalized diffusivity,  $D$ , of rigid chains of type A versus energy,  $E$ , for different periods of the periodic potential. The dashed line corresponds to the theoretical result according to equation (4) for  $T = 400$ . Curves of theoretical results of equation (4), for different values of  $T$  ( $100 < T < 3200$ ), are indistinguishable. The solid line indicates a slope of  $-1$ . Monte Carlo results were obtained averaging over 1000 samples with  $\delta = 0.18$ .

agreement with the Monte Carlo results shown in figure 5 for chains of type A (where the analytical result of equation (4) for  $T = 400$  is shown in a dashed line).

On other hand for the point model A–B, one can obtain that  $D$  is given by (see appendix)

$$D = \frac{T^2}{\left(\frac{T}{2} - 1\right) \left[4\left(\frac{T}{2} - 2\right) + 6e^{E/2} + 2e^{-E/2} + 4\right] + 2(1 + e^E)}. \quad (5)$$

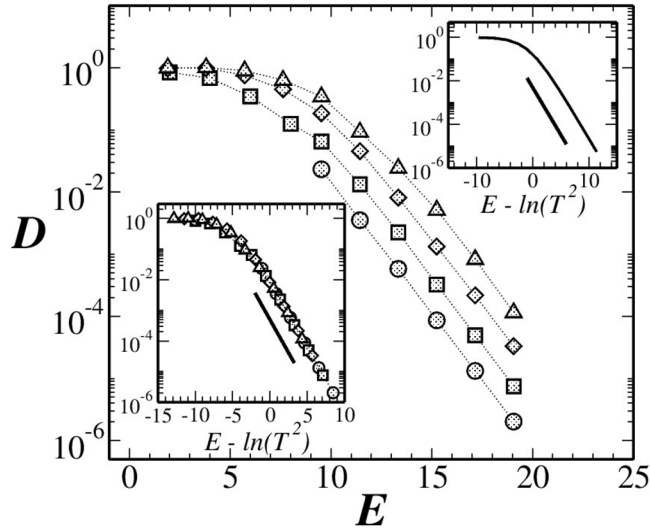
The normalized diffusivity given by equation (5) is shown, as a function of  $(E - \ln T^2)$ , in the inset of figure 6 for  $T = 100, 200, 400, 800$ . It is observed that the normalized diffusivity eventually adopts an exponential dependence with  $E$  and for large values of  $E$  and  $T$ ,  $D$  decreases as  $T^2 \exp(-E)$  (see equation (5)). This behavior is in agreement with the Monte Carlo results shown in figure 6 for chains of type A–B.

In this section, we introduced two simple models that surprisingly present different trends regarding diffusion. These models consist of a single particle diffusing along a string with non-equivalent sites in a periodic arrange. The exponential decay are  $\exp(-E)$  and  $T^2 \exp(-E)$  for chains A and Chains A–B respectively. The term  $T^2$  makes a strong difference between both behaviors.

## 5. Final remarks

For a given substrate (characterized by a value of  $\delta$ ) of period  $T$ , the more important results obtained for normalized diffusion constant  $D$  are the following.  $D$  versus  $N$  is a periodic function of period  $T$  ( $2T$ ) for chains of type A (type A–B, respectively), and





**Figure 6.** Normalized diffusivity,  $D$ , of rigid chains of type A–B versus energy,  $E$ , for different periods of the potential. Circles correspond to  $T = 200$ , squares to  $T = 400$ , diamonds to  $T = 800$  and triangle up to  $T = 1600$ . The bottom inset shows the same data from the main figure but with a rescaled horizontal axis,  $E - \ln(T^2)$ . The upper inset shows the theoretical results of  $D$  according to equation (5) for  $T = 200$  to  $T = 1600$ . Note that the curves of theoretical results of equation (5), are indistinguishable for different values of  $T$ . Solid lines in the insets indicates a slope of  $-1$ . Monte Carlo results were obtained averaging over 1000 samples with  $\delta = 0.18$ .

present minimum values at  $N = (m + 1/2)T$  [ $N = (2m + 1)T$ ], where  $m = 0, 1, 2, 3, \dots$  for chains of types A (type A–B, respectively).

We then studied the short chain regime in which  $D$  is far from its first minimum value, that is, when  $N \ll T/2$  for chains of type A and when  $N \ll T$  for chains of type A–B. In this regime we found relevant the variable  $X = N\delta$ . Indeed,  $D$  is a universal function of  $X$ , where  $X = E$  for chains of type A and  $X = (E - \ln T^2)$  for chains of type A–B. In both cases,  $D \approx 1$  for small values of  $X$  and  $D \propto \exp(-X)$  for large values of  $X$ . These two behaviors have been obtained from Monte Carlo simulation and have been checked analytically with simplified point particle models. On the other hand, for rigid chains the same kind of behavior was obtained from Monte Carlo simulation using the following jumping rates

$$k = (k_0/N) \exp[-(E_f - E_i)/2], \text{ for all } E_f \text{ and } E_i, \quad (6)$$

instead of the jumping rates given by equation (1). This implies that the general trends are universal, independent of the microscopic rules of the model.

Let us now consider the connection with experimental results for the diffusion of copolymers of two blocks (diblock copolymers) in a lamellar structure composed of ordered copolymers of the same type [15]. Regularly, a normalized diffusion coefficient in the perpendicular direction to the interface,  $D = D_c/D_0$ , is computed, where  $D_0$  is the diffusion coefficient in the absence of potential fields. The normalized diffusion coefficient is found to present a universal dependence, having an exponential decrease with the product  $\chi N$  above a certain value, where  $\chi$  is the thermodynamic interaction

parameter between units of the two blocks and  $N$  is the number of segments. The exponential dependence was attributed to the thermodynamic barrier that individual block copolymer chains experience as they move through the copolymer ordered structure. This universal dependence and the exponential decay are in agreement with the theoretical results obtained in the initial regime for chains of type A–B (the parameter  $\chi$  play the role of  $\delta$  in the model). Within our knowledge, the experimental results are usually obtained for a fixed period  $T$  and then, the universal behavior means that the results only depend on  $E = N\delta$ . Our model would represent a medium with a strong segregation where the interfacial width between region I and region II is much smaller than the period  $T$ .

Since many mechanisms that are present in real systems are not included, we do not attempt to reproduce specific experimental results; this is a simple model to study the effect of periodic potentials on chain diffusion. However, the model reflects the main characteristics observed in experiments, as the universal dependence of diffusion with the product  $\chi N$ . Among relevant details not incorporated in our model, we can mention the chain flexibility and the thermal fluctuations of the interface.

It is expected that broadening the interfacial width in block copolymers would increase diffusion. Indeed, when the interface between the domains is broad, both blocks mix at the interface increasing the energy of the ground state and reducing the energy of the activated states. Consequently the difference between the ground and activated states is reduced favoring diffusion. From the analysis of this effect one can conclude that the results will have the same global behavior as that shown in figure 6.

The effects of chain flexibility were tested with the necklace model [6] adapted for copolymers, with  $N/2$  particles A and  $N/2$  particles B. Computational simulations with the necklace model are very time consuming and then we tested chain diffusion for not very long periods  $T$ . Anyway, it is apparent that the general behavior is similar for both cases indicating that the diffusion of rigid chains contains the basic mechanisms responsible for the observed general trends.

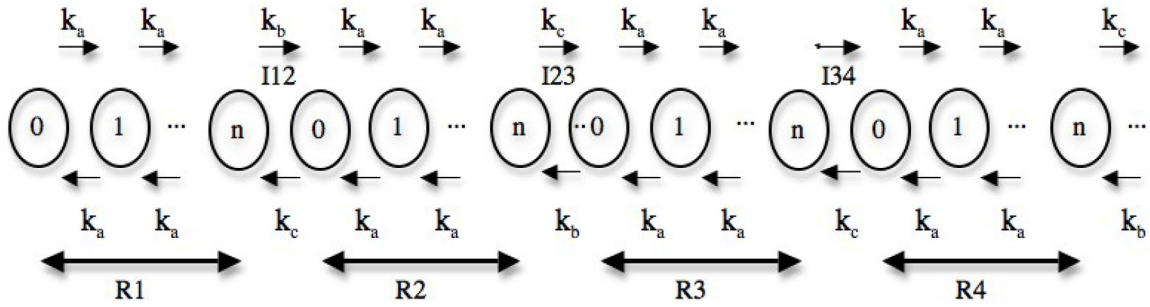
## Acknowledgments

This work was partially supported by the National Council for Scientific and Technical Research (CONICET) of Argentina (PIP 2015-2017 No 0021), and the National University of Mar del Plata (Argentina).

## Appendix

In order to visualize the origin of the universal dependence of the normalized tracer diffusion coefficient of chain diffusion, in periodic potentials, we introduce very simple models that present the observed trends emerging naturally. Our models are based on a single particle diffusing along a string with inequivalent sites. We model this with a square periodic potential as shown in figure A1. This simplification has a reward, the exact solution can be found resorting to a steady-state approach (see [18]).

We assume a steady-state situation with a constant diffusive flux along the string from right to left and the first site empty, as seen in figure A1. The key to find out the



**Figure A1.** Schematic representation for the diffusion of a particle in a 1D periodic potential resembling the diffusion of chains of type A as in figure 1(b). Jumping rates are denoted as  $k$ 's, and ovals represent sites.

diffusivity consists in finding the particle flux  $F$  along the string. In region 1,  $R1$ , the flux from right to left is given by

$$F = k_a c_{1,i+1} - k_a c_{1,i}, \tag{A.1}$$

where  $c_{i,j}$  is the number of particles in a site; the first subscript denotes the region and the second one the site on that region. Since this flux has to be the same along the string, it must be equal to  $k_a c_{1,1}$ . Thus, the number of particles in any site of  $R1$  is

$$c_{1,i} = i c_{1,1}. \tag{A.2}$$

At the first interface,  $I12$ , the flux is

$$F = k_c c_{2,0} - k_b c_{1,n}. \tag{A.3}$$

Thus, knowing that the flux must be  $k_a c_{1,1}$ , the number of particles at the first site of  $R2$  can be determined

$$c_{2,0} = \frac{k_b}{k_c} n c_{1,1} + \frac{k_a}{k_c} n c_{1,1}. \tag{A.4}$$

Following this way of thinking, the number of particles in regions 2, 3, and 4 can be deduced

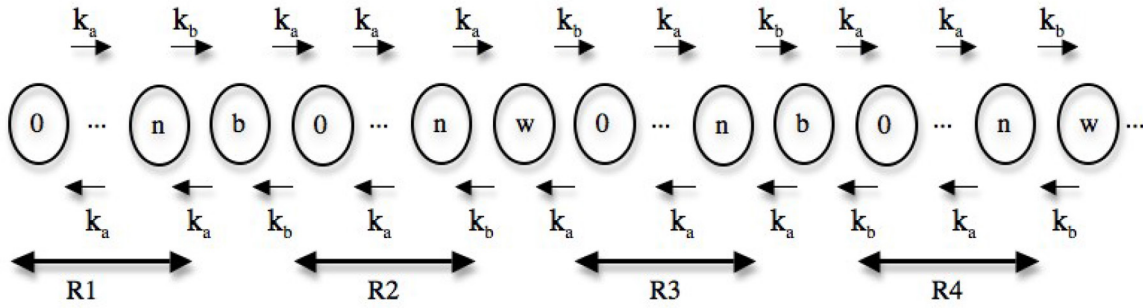
$$c_{2,i} = \left( n \frac{k_b}{k_c} + \frac{k_a}{k_c} + i \right) c_{1,1} \tag{A.5}$$

$$c_{3,i} = \left( n + 2 \frac{k_a}{k_b} + n \frac{k_c}{k_b} + i \right) c_{1,1} \tag{A.6}$$

$$c_{4,i} = \left( n + 2n \frac{k_b}{k_c} + 3 \frac{k_a}{k_c} + i \right) c_{1,1}. \tag{A.7}$$

Due to translation symmetry, the unit cell contains a couple of regions. Then, we can apply Fick's law between two cells: cell 1 corresponding to  $R1$  and  $R2$ , and cell 2 corresponding to  $R3$  and  $R4$ . The number of particles in cell 1,  $N_1$ , is

$$N_1 = \sum_{i=0}^n i c_{1,1} + \sum_{i=0}^n \left( n \frac{k_b}{k_c} + \frac{k_a}{k_c} + i \right) c_{1,1} \tag{A.8}$$



**Figure A2.** Schematic representation for the diffusion of a particle in a 1D periodic potential resembling the diffusion of chains of type A–B as in figure 2(c). Jumping rates are denoted as  $k$ 's, ovals represent sites,  $b$  is a site at a barrier, and  $w$  a site at a well.

and the number of particles in cell 2,  $N_2$ , is

$$N_2 = \sum_{i=0}^n \left( n + 2\frac{k_a}{k_b} + n\frac{k_c}{k_b} + i \right) c_{1,1} + \sum_{i=0}^n \left( n + 2n\frac{k_b}{k_c} + 3\frac{k_a}{k_c} + i \right) c_{1,1}. \quad (\text{A.9})$$

With equations (A.8) and (A.9), the difference  $N_2 - N_1$  can be calculated

$$N_2 - N_1 = \left( 2n + 2\frac{k_a}{k_c} + 2\frac{k_a}{k_b} + n\frac{k_c}{k_b} + n\frac{k_b}{k_c} \right) (n + 1)c_{1,1}. \quad (\text{A.10})$$

Finally, we apply Fick's law between cells, so that

$$F = k_a c_{1,1} = D \frac{N_2 - N_1}{[2(n + 1)]^2}, \quad (\text{A.11})$$

where the particle density in a cell is the number of particles divided the cell size,  $2(n + 1)$ . With equations (A.10) and (A.11), the diffusivity is

$$D = \frac{4(n + 1)k_a}{\left( 2n + 2\frac{k_a}{k_c} + 2\frac{k_a}{k_b} + n\frac{k_c}{k_b} + n\frac{k_b}{k_c} \right)}, \quad (\text{A.12})$$

where the distance between sites was adopted to be 1. For the first chain model [see figure 1(b)], the ratio between jumping rates can be written as follows

$$\begin{aligned} \frac{k_b}{k_c} &= \exp(-E) \\ \frac{k_a}{k_b} &= \exp(E) \\ \frac{k_a}{k_c} &= 1, \end{aligned} \quad (\text{A.13})$$

where energies are in terms of  $k_B T_0$ . With this, equation (A.12) takes the form

$$D = \frac{4(n + 1)k_a}{2n + 2 + 2\exp(E) + n\exp(E) + n\exp(-E)}. \quad (\text{A.14})$$

In terms of the potential period  $T = 2(n + 1)$ , equation (A.14) can be written as

$$\frac{D_c}{D_0} = \frac{2T}{T + \left(\frac{T}{2} + 1\right) \exp(E) + \left(\frac{T}{2} - 1\right) \exp(-E)}, \quad (\text{A.15})$$

which is equation (4) in the text.

In the second model we have barriers and wells as shown in figure 2(c). This model can also be solved applying the steady-state method of [18]. Following similar steps as those for the first model, see figure A2, the diffusivity can be deduced:

$$D = \frac{[2(n+2)]^2 k_a}{(n+1) \left(4n + 6\frac{k_a}{k_b} + 2\frac{k_b}{k_a} + 4\right) + 2 \left(1 + \left(\frac{k_a}{k_b}\right)^2\right)}. \quad (\text{A.16})$$

For this model (see figure 2(c)), the ratio between jumping rates are those of equation (A.13) replacing  $E$  by  $E/2$ . Finally, in terms of the potential period, in this case  $T = 2(n+2)$ , equation (A.16) can be written as

$$D = \frac{T^2}{\left(\frac{T}{2} - 1\right) \left[4 \left(\frac{T}{2} - 2\right) + 6e^{E/2} + 2e^{-E/2} + 4\right] + 2(1 + e^E)}, \quad (\text{A.17})$$

which is equation (5) in the text.

The analytical results of equations (A.15) and (A.17) were verified with Monte Carlo simulation for the point model A and the point model A–B, respectively.

## References

- [1] de Gennes P G 1979 *Scaling Concepts in Polymer Physics* (Ithaca, NY: Cornell University Press)
- [2] Doi M and Edwards S F 1986 *The Theory of Polymer Dynamics* (Oxford: Clarendon)
- [3] Colby R H and Rubinstein M 2003 *Polymer Physics* (Oxford: Oxford University Press)
- [4] Lodge T P 1999 *Phys. Rev. Lett.* **83** 3218
- [5] Viovy J L 2000 *Rev. Mod. Phys.* **72** 813
- [6] Terranova G R, Aldao C M and Martín H O 2007 *Phys. Rev. E* **76** 031111
- [7] Choi S, Bates F S and Lodge T P 2011 *Macromolecules* **44** 3594
- [8] Nikoubashman A, Register R A and Panagiotopoulos A Z 2013 *Soft Matter* **9** 9960
- [9] Matsen M W 2002 *J. Phys.: Condens. Matter* **14** R21–47
- [10] Barrat J L and Fredrickson G H 1991 *Macromolecules* **24** 6378
- [11] Lodge T P and Dalvi M C 1995 *Phys. Rev. Lett.* **75** 657
- [12] Fredrickson G H and Bates F S 1996 *Annu. Rev. Mater. Sci.* **26** 501
- [13] Cavicchi K A and Lodge T P 2003 *Macromolecules* **36** 7158
- [14] Hamersky M W, Tirrell M and Lodge T P 1998 *Langmuir* **14** 6974
- [15] Yokoyama H 2006 *Mater. Sci. Eng. R* **53** 199
- [16] Wang M, Alexander-Katz A and Olsen B D 2012 *ACS Macro Lett.* **1** 676  
Wang M, Timachova K and Olsen B D 2013 *Macromolecules* **46** 1651  
Wang M, Timachova K and Olsen B D 2013 *Macromolecules* **46** 5694  
Wang M, Likhtman A E and Olsen B D 2015 *ACS Macro Lett.* **4** 242  
Wang M, Timachova K and Olsen B D 2015 *Macromolecules* **48** 3121
- [17] Eurich F, Karatchentsev A, Baschnagel J, Dieterich W and Maass P 2007 *J. Chem. Phys.* **127** 134905
- [18] Aldao C M, Iguain J L and Martín H O 1996 *Surf. Sci.* **366** 483