Exact diffusion coefficient for a chain of beads in one dimension using the Einstein relation

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The one-dimensional motion of a chain of N beads is studied to determine its diffusion coefficient. We found an exact analytical expression for all N through two methods by resorting to the Einstein relation. Results are tested with the help of Monte Carlo simulations.

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A chain in one dimension can move by contracting and stretching in a wormlike fashion. This mechanism, named reptation in polymer physics, plays a key role in the dynamics of entangled polymer melts and, in a similar manner, in the electrophoresis of DNA molecules [1,2]. In the dynamics of entangled polymers, neighboring chains constrain a given chain to diffuse only along a confining tube and then the chain executes a one-dimensional random walk [3–7]. Thus, a chain can progress by leaving part of the initial tube and creating a new part as it reptates.

The model, as originally introduced, predicts that diffusivity scales with the molecular weight as $M^{-\alpha}$, where $\alpha=2$ in three dimensions. While a reptating chain moves along its tube in space this motion corresponds to a much smaller displacement because the tube is contorned; it can be shown that for the one-dimensional diffusivity along the tube $\alpha=1$.

In this paper we discuss a model we introduced recently that describes a chain diffusing in one dimension [8]. The dynamics is similar to that described in the original work of de Gennes [3]. However, in our model particles do not have all the same mobility. To determine diffusivity and mobility of such a chain is the main goal of the present paper.

We consider a chain in a one-dimensional lattice consisting of N particles that can hop to the nearest site only if this site is empty. Particles can hop to the right or left but no more than a site can be empty between two particles, a rule that maintains the integrity of the chain. Particles located at the end of the chain have different behavior than the rest. Indeed, if allowed by the above rules, a middle particle jumps with a probability per unit time p_c while end particles are allowed to jump with probabilities per unit time p_a and p_b when jumping stretches or compresses the chain, respectively. Hence, p_a, p_b, and p_c are the free parameters in this model [9]. In the following we use that the distance a between adjacent sites of the lattice is equal to 1.

An empty site in the chain is named a hole. A hole is created or annihilated every time an end particle jumps moving away from the chain or towards the chain. An end particle jumping attempt that creates a hole is successful with probability $p_a(1-P_h)$, where P_h is the hole probability. Similarly, an end particle jumping attempt that annihilates a hole succeeds with probability p_bP_h. In equilibrium we expect the same probability for creation and annihilation. Then, P_h can be expressed as

$$P_h = \frac{p_a}{p_a + p_b}. \tag{1}$$

Rubinstein introduced a model in which the chain also consists of N connected elements, the reptons [10]. The integrity of the chain is maintained by not allowing moves that vacate a site. Also, the original order of the reptons is preserved and thus a repton can move only if it is an end member of the reptons that occupy the same cell. The model has a parameter z that reflects the dimension of the problem. z is the number of possible gates for an end repton to move. Then, there are $z-1$ possible gates to enter into an empty cell and only one gate to move into an already occupied one. For one dimension $z=2$ and for three dimensions $z=6$, which can be understood to correspond to a three-dimensional cubic lattice. Hence, at the end of the chain the probability of a move that lengthens the configuration must be $(z-1)$ times the probability that shortens it. Thus, the probability of all moves are $1/z$, except those of the end reptons that lengthen the chain that are $(z-1)/z$.

The rules of our model are different from those of the repton model of Rubinstein, but there is a direct correspondence between both models regarding diffusion. The main difference between both models is the flexibility we adopted regarding the possible different jump probabilities for particles at the end of chains. Indeed, it is readily seen that the Rubinstein model corresponds to our model by making $p_b=p_c=1/z$ and $p_a=(z-1)/z$.

We recently attempted to derive exact analytical expressions for the diffusivity in our model and were only successful for a chain with two and three beads [9]. We used an approach not regularly applied in the literature that simplifies the calculations and the problem could be solved using only algebra [11,12]. The method consists in applying Ficks's first law for a large number of noninteracting chains diffusing in steady state. The method requires the analysis of all possible chain configurations and then it becomes intractable for $N>3$. In what follows, after a general discussion, we will introduce two approaches that, resorting to the Einstein relation, lead to the exact analytical form for the chain diffusivity for all N.

First we will discuss some basic ideas in the simple case of a single diffusing particle. The diffusion coefficient D is given by

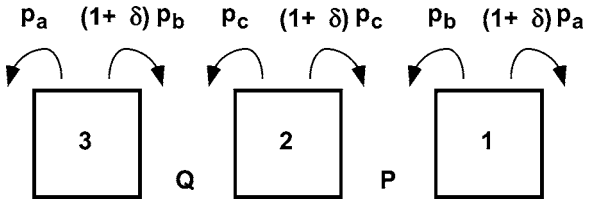

FIG. 1. Chain of three beads and jumping probabilities when the same force is applied to every bead. P is the probability of finding a hole between particles 1 and 2 and Q is the probability of finding a hole between particles 2 and 3.

$$D = ka^2, \tag{2}$$

where k is the jumping frequency, to the right or to the left, between nearest neighbor lattice sites separated by a distance a. Let us consider next the asymmetric case in which the jumping frequencies to the right and to the left are $(1+\delta)k$ and k, respectively ($\delta > 0$). If so, the particle moves to the right with drift velocity v given by

$$v = a\delta k. \tag{3}$$

To derive the Einstein relation we consider a small potential gradient and then a small force F acting on the particle to the right. With $\delta \ll 1$ we can write

$$1 + \delta = \exp(\Delta V/k_B T) \cong 1 + \Delta V/k_B T = 1 + Fa/k_B T. \tag{4}$$

The mobility μ is defined as the ratio between drift velocity and force. Thus

$$v = \mu F. \tag{5}$$

With Eqs. (2)–(4) the Einstein relation is obtained:

$$\mu = \frac{D}{k_B T}. \tag{6}$$

For the sake of simplicity, we can define a mobility μ' through the equation

$$v = \mu' \delta. \tag{7}$$

Accordingly, the Einstein relation adopts the form

$$\mu' = D/a. \tag{8}$$

For $\delta \ll 1$, δ is proportional to the force F and the validity of Eq. (6) implies the validity of Eq. (8) (i.e., both relations are equivalent). Note that the standard Einstein relation is only valid for small values of F (strictly speaking in the limit $F \to 0$). Conversely, in the present simple case, Eq. (8) holds for any value of δ. In the following we will refer to Eqs. (6) and (8) as the Einstein relation and δ as the "force" acting on a bead.

In Fig. 1 we show a chain of three beads in which a force is applied to all beads. P and Q are the probabilities of finding a hole between particles 1 and 2 and between particles 2 and 3, respectively. With no force applied, P and Q adopt the value given by Eq. (1). We will see that, in general, this is not the case. When a force to the right is applied as shown in Fig. 1, the average velocity of the beads to the right can be expressed, within a mean field approach, as

$$v_1 = (1+\delta)p_a(1-P) - p_b P, \tag{9}$$

$$v_2 = (1+\delta)p_c(1-Q)P - p_c(1-P)Q, \tag{10}$$

$$v_3 = (1+\delta)p_b Q - p_a(1-Q), \tag{11}$$

where v_1, v_2, and v_3 are the velocities for particles 1, 2, and 3 of the chain. Since all particles must have the same drift velocity, $v_1 = v_2 = v_3 = v$. From Eqs. (9) and (11), P and Q can be expressed as follows:

$$P = \frac{(1+\delta)p_a - v}{(1+\delta)p_a + p_b}, \tag{12}$$

$$Q = \frac{p_a + v}{p_a + (1+\delta)p_b}. \tag{13}$$

For small forces, $\delta \ll 1$ and then $v = O(\delta)$, Eqs. (12) and (13) can be written at order δ as

$$P = \frac{p_a}{p_a + p_b}(1 + \Delta), \tag{14}$$

$$Q = \frac{p_a}{p_a + p_b}(1 - \Delta), \tag{15}$$

where

$$\Delta = \frac{p_b}{p_a + p_b}\delta - \frac{v}{p_a}. \tag{16}$$

With Eq. (10) and the help of Eqs. (14)–(16), the velocity can be derived to be

$$v = \frac{3\delta p_a p_b p_c}{(p_a + p_b)(p_a + p_b + 2p_c)}. \tag{17}$$

It can be shown that correlations between holes are present in a field but they are null at order δ and then the mean field assumption is valid. Finally, since the total force applied to the chain is 3δ, using the Einstein relation, the diffusivity adopts the form

$$D = \frac{p_a p_b p_c}{(p_a + p_b)(p_a + p_b + 2p_c)}, \tag{18}$$

which is the same result obtained in Eq. (20) of Ref. [9].

It is straightforward to extend this method to longer chains. From a quick inspection of the expressions resulting for chains of different length, the general expression for the diffusivity can be inferred to be

$$D = \frac{p_a p_b p_c}{(p_a + p_b)[(N-2)(p_a + p_b) + 2p_c]}, \tag{19}$$

which is valid for $N \geqslant 2$. In Fig. 2, numerically calculated diffusion coefficients and theoretical results using Eq. (19) are shown. The agreement is remarkable. Note that for $p_a + p_b = p_c$ the diffusivity adopts the value $p_a p_b / p_c N$.

For the special case that corresponds to the Rubinstein model, $p_a = (z-1)/z$, and $p_b = p_c = 1/z$. The diffusivity in this model, D_R, adopts the form

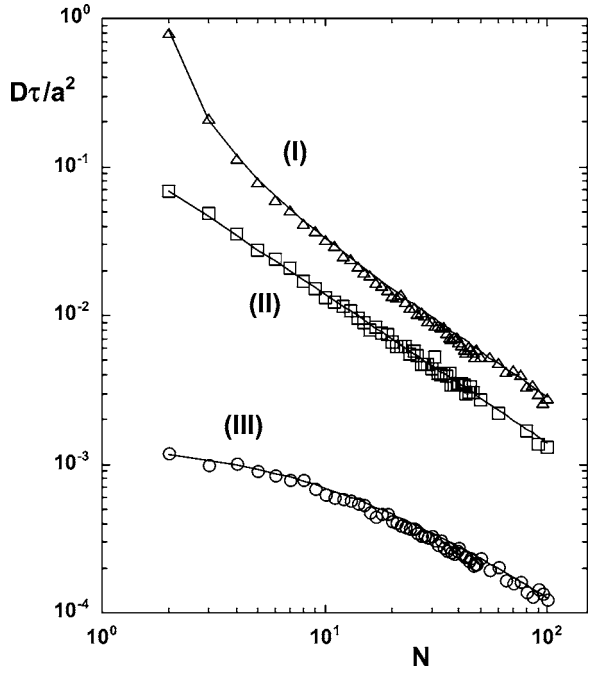

FIG. 2. Diffusion coefficient of the center of mass for chains consisting of N beads. The parameters of the model $(p_a\tau, p_b\tau, p_c\tau)$ are $(1, \frac{1}{5}, \frac{1}{5})$ for case I, $(\frac{5}{6}, \frac{1}{6}, 1)$ for case II, and $(\frac{5}{36}, \frac{1}{36}, 1)$ for case III, where τ is the unit time. Symbols correspond to Monte Carlo results and lines to theoretical results according to Eq. (19). For the sake of clarity, diffusivity values for case I were multiplied by 10 and those for case III by 0.1.

$$D_R = \frac{z-1}{(N-2)z^3 + 2z^2}. \tag{20}$$

This result is in agreement with the numerically calculated diffusivities and the asymptotic result reported in Ref. [10].

We found a much simpler method to figure out the coefficient of diffusivity for our model. In the reptation theory, as originally presented by de Gennes, all beads have the same behavior [1,3]. Then, the frictional force is proportional to the number of beads in the chain. Hence, the mobility μ must be equal to μ_1/N, where μ_1, independent of N, is the mobility of a single bead. If the Einstein relation is valid, then the one-dimensional diffusion coefficient or tube diffusion must scale as $1/N$.

Interestingly, the above arguments can be extended to chains with beads of different mobility. An external force, F_{ext}, on a chain is directly related to the drift velocity through the mobility μ as $v = \mu F_{ext}$. The external force is the sum of the forces applied to every bead, F_i. We propose that forces on a particular bead can have an external origin, F_{iext} (for example, due to an external electric field if beads are charged) or an internal origin from its neighbors' beads. Thus, for any bead the following equation is valid,

$$v_i = \mu_i F_{itot}, \tag{21}$$

where F_{itot} is the sum of the external plus internal forces acting on the bead. Thus, we can write

$$\frac{1}{\mu} = \sum_i \frac{F_{iext}}{v} = \sum_i \frac{F_{itot}}{v} = \sum_i \frac{1}{\mu_i}, \tag{22}$$

since the sum of all internal forces must vanish and the drift velocity of the chain and of any bead must be the same.

Equation (22) constitutes the key to solve this type of problem. Next, the values of μ_i are needed to be found. To do it, we can resort to the Einstein relation. Instead of the mobility, we can determine the diffusivity of the beads within the chain that can be figured out through the mean jumping frequency using Eq. (2).

In our model, the mean jumping frequencies can be readily calculated. On average, the probability that an end particle performs a jump, and then the mean jumping frequency, is

$$k_e = (1 - P_h)p_a = P_h p_b, \tag{23}$$

while for a middle particle, the mean jumping frequency is

$$k_m = (1 - P_h)P_h p_c. \tag{24}$$

With Eq. (1), k_e and k_m can be expressed as

$$k_e = \frac{p_a p_b}{p_a + p_b}, \tag{25}$$

$$k_m = \frac{p_a p_b p_c}{(p_a + p_b)^2}. \tag{26}$$

Finally, using Eq. (22) the mobility and then the diffusivity for the chain can be figured out,

$$\frac{1}{D} = \sum_i \frac{1}{D_i} = \frac{2}{\frac{p_a p_b}{p_a + p_b}} + \frac{N-2}{\frac{p_a p_b p_c}{(p_a + p_b)^2}}, \tag{27}$$

an expression that can be readily rearranged to take the form of Eq. (19).

It is clarifying to elaborate on the meaning of the proposed internal forces. Let us focus on the simple chain of three beads of Fig. 1. In the general case in which the mobility of the middle bead is different from that of the end beads, an external force evenly applied to the three beads would imply different drift velocities. Obviously, this is not possible because the chain would lose integrity. Then, how is it possible that the beads are dragged with the same drift velocity? The answer to this question is in Eqs. (14) and (15). As the chain is dragged it deforms. The chain deformation is responsible for the drift velocity being the same for every bead.

If $p_a + p_b > p_c$, the mobility of end beads is greater than that of the middle bead [see Eqs. (25) and (26)] and, from Eqs. (16) and (17), $\Delta > 0$. Thus, P becomes larger and Q smaller related to their values when no force is applied. As a consequence, the middle particle increases its drift velocity and end particles reduce theirs [see Eqs. (9)–(11)]. If $\Delta < 0$, the mobility of the middle bead is smaller that that of the end beads; then P becomes smaller and Q larger so that the drift velocities of all the particles become the same.

When $p_a+p_b=p_c$, it can be seen, from Eqs. (25) and (26), that the mobilities of all the beads are the same and equal to $p_a p_b/p_c$. In this case, P and Q always adopt the same value, that corresponding to equilibrium, Eq. (1). This means that the chain is dragged without deforming (i.e., without any internal force). It can be easily shown that this is valid for a chain of any length. Indeed, the velocity for a general middle bead i in a chain of any length is

$$v_i = (1+\delta)p_c(1-Q)P - p_c(1-P)Q, \tag{28}$$

where P and Q correspond to the probability of having a hole at the right and left of the bead, respectively. If $p_a+p_b=p_c$, then Eq. (28) is satisfied with $v_i=\delta p_a p_b/p_c$ and $P=Q=p_a/(p_a+p_b)$ independently of the value of δ. Since this is a general equation for any middle bead, the probability of having a hole at any possible site must be the same and equal to that of equilibrium. Thus, when the same force is applied to every bead, chains of any length are dragged without deforming and the Einstein relation is always valid. In other words, the drift velocity is proportional to δ for any value of δ.

So far, we considered that the same force was applied to every bead. However, if this is not the case and $|\delta_i| \ll 1$, where δ_i denotes the force applied to bead i, the drift velocity of the chain is always equal to

$$v = D\sum_i \delta_i. \tag{29}$$

In summary, using the Einstein relation we could find an analytical solution for a type of model that simulates the diffusion of a chain of particles in one dimension. In particular, the second approach we have introduced is very easy to apply to a variety of situations. We mean that the mobility of the beads that form the chain might take any value. We have checked, for example, that this approach is valid for a case in which end particles have different mobilities and also for a chain with middle particles having different jumping probabilities per unit time, p'_{ci}. These results were all tested with the help of Monte Carlo simulations. Thus, the diffusivity, in the most general manner, can be written as

$$D = \frac{p_{a1}p_{bN}p'_c}{(p_{aN}+p_{bN})\left(\left(1+\frac{p_{b1}}{p_{bN}}\right)p'_c + (p_{a1}+p_{b1})\right)}, \tag{30}$$

where p'_c is given by

$$\frac{1}{p'_c} = \sum_{i=2}^{N-1} \frac{1}{p_{ci}}, \tag{31}$$

p_{a1} and p_{b1} correspond to one end particle, and p_{aN} and p_{bN} to the other one. Note that p_{a1}/p_{b1} must be equal to p_{aN}/p_{bN} if there are no external forces.

Note added in proof. In a recent paper [13], the author determines, through a different method than ours, the exact curvilinear diffusion coefficient in the repton model. His results are in accordance with the present work.

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