Single-File Diffusion on a Periodic Substrate

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An assembly of "nonpassing" particles diffusing on a one-dimensional periodic substrate is shown to undergo single-file diffusion for both noiseless (ballistic) and stochastic dynamics. The dependence of the corresponding diffusion coefficients on the density and temperature of the particles and on the substrate parameters is determined by means of numerical simulations and analytically interpreted within the formalism of standard Brownian motion.

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As the direct observation of cellular flows and the operation of biology inspired nanodevices are becoming experimentally more and more accessible, understanding particle diffusion in a 1D system has been recognized as a key issue in transport control [1]. When pumping a dilute mixture of interacting particles through a narrow channel, either by applying external (dc or ac) gradients or by rectifying ambient fluctuations, the efficiency of the transport mechanism is largely influenced by the diffusion of the pumped particles [1,2].

Most literature on the diffusion of suspended particles rests upon many-body techniques borrowed from well established theories, like hydrodynamics and other kinetic theories [3]. An alternate approach to this problem consists in assuming that all particles are subjected to spatially uncorrelated thermal fluctuations at the appropriate temperature so that they can be treated as independent Brownian particles (as long as hydrodynamic interactions are negligible [3,4]). Formalisms based on the Langevin equation and on the Fokker-Planck equation can then be developed to compute numerically and analytically the relevant particle currents and their dispersion [5].

In this context the characterization of the interparticle interaction plays a central role. If the particles are able to pass one another, the interparticle collisions are responsible for a number of rectification mechanisms [6–8], including gating, harmonic mixing, and Stokes' drag. All of this is in addition to the rectification effects possibly induced by the spatiotemporal asymmetries in the particle coupling to their environment (ratchet effect [9]). Markedly different are the so-called "nonpassing" flow geometries: suppressing particle hopping makes the subdiffusive nature of a single-file system emerge in the case of both elastic [10] and inelastic collisions [11].

Here we consider a file of N unit-mass particles moving with preassigned dynamics along a segment of length L; if the particle-particle interaction is hard core (with zero radius), the elastic collisions between neighboring particles are nonpassing—meaning that the particles can be labeled according to an ordered sequence. This implies that the file is geometrically constrained and the long-time diffusion of an individual particle strongly suppressed [12–14].

In the present Letter we characterize the diffusive motion of a single file drifting on a periodic substrate subject to either ballistic or stochastic dynamics. Remarkable, in our view, is the case of stochastic single files constrained on a periodic substrate. In the absence of geometric constraints, dilute mixtures of suspended interacting particles are known to exhibit normal diffusion, no matter what the substrate [15]; when driven by an external force their diffusion constant gets enhanced, the excess diffusion signaling particle depinning from the substrate or cluster fragmentation [16,17]. In contrast, an assembly of nonpassing particles is shown here to exhibit anomalous diffusion with exponent $\frac{1}{2}$ independent of the substrate. The dependence of the diffusion coefficients of a single file on both the file and the substrate parameters is *quantitatively* reproduced by simple analytical laws.

The diffusion of a free single file (SF), i.e., in the absence of a substrate, has been investigated in detail [12–14,18]. In the thermodynamic limit ($L, N \to \infty$ with constant density $\rho \equiv N/L$) the mean square displacement of each file particle can be written as

$$\langle \Delta x^2(t) \rangle = \langle |\Delta x(t)| \rangle / \rho \tag{1}$$

with $\langle |\Delta x(t)| \rangle$ denoting the absolute mean displacement of a free particle. For a *ballistic* single file (BSF), clearly $\langle |\Delta x(t)| \rangle = \langle |v| \rangle t$, where $\langle \cdots \rangle$ is the ensemble average taken over the distribution of the initial velocities, and therefore

$$\langle \Delta x^2(t) \rangle = \langle |v| \rangle t / \rho. \tag{2}$$

A BSF particle diffuses apparently like a Brownian particle with normal diffusion coefficient $D = \langle |v| \rangle / (2\rho)$. For a *stochastic* single file (SSF) of Brownian particles with damping constant η at temperature T, the equality $\langle |\Delta x(t)| \rangle = \sqrt{4D_0 t/\pi}$ yields the anomalous diffusion law

$$\langle \Delta x^2(t) \rangle = 2F\sqrt{t}/\rho, \tag{3}$$

where the mobility factor $F = \sqrt{D_0/\pi}$ is related to the single particle diffusion constant $D_0 = kT/\eta$, and $\langle \cdots \rangle$ involves an additional stochastic average. The normal (2) and the subdiffusive (or SF) regimes (3) have been confirmed both numerically [14,19] and experimentally [20,21]; the crossover between these two regimes has also been investigated [10].

In the following we address the case of a SF diffusing on a sinusoidal substrate with potential:

$$V(x) = d\left(1 - \cos\frac{2\pi x}{l}\right). \qquad (4)$$

Extensive numerical simulations have been carried out for both BSF and SSF. The first to investigate this problem was Percus [22], who developed a grand potential approach to the equilibrium statistical mechanics of a SF of elastic particles with diameter a (for an extension of Percus' formalism to an inelastic SF see Ref. [23]). Note that this variation of the SF model rises quite naturally in connection with most quasi-1D systems where the particles are represented by spheres of diameter a moving along a narrow channel with average cross section σ, such that $\sigma < a$; the walls, say, of a nanotube or a zeolite pore are more likely to be periodically corrugated than straight [18].

Ballistic single file.—In the simulations of Fig. 1 each particle is assigned random initial position and velocity; upon each elastic collision it switches velocity with either neighbor without altering the file labeling. Moreover, we expect that adding the substrate potential (4) has no impact on the normal diffusion law (2); only the relevant diffusion coefficient ought to be reduced [15]. Let us denote by α, $0 \leq \alpha \leq 1$, the fraction of particles with total energy E larger than the potential barrier $2d$. Our simulations clearly show that $\langle \Delta x^2(t) \rangle$ obeys asymptotically law (2) with D proportional to α [Fig. 1(a)].

Here, the αN running particles with $E > 2d$ were picked at random and so was their position on the substrate; their energy was set equal to one value E_α, the same for all, while the energy of the $(1-\alpha)N$ particles trapped in the potential wells was set to zero; the additional constraint $\langle v \rangle = 0$ on the velocity of the file center of mass was imposed for convenience. Note that assigning the energy E_i to the ith particle at random, according to a broader distribution $g(E_i)$ with $\langle E_i \rangle = \alpha E_\alpha$, turns out to be statistically equivalent [Fig. 1(b)]. Moreover, the diffusion coefficient is independent of the substrate period l (not shown) and inverse proportional to the density ρ [Fig. 1(c)].

The numerical results of Fig. 1 can be summarized by rewriting the diffusion law (2) for a BSF as

$$\langle \Delta x^2(t) \rangle = \langle |\bar{v}| \rangle t/\rho, \qquad (5)$$

where $\langle |\bar{v}| \rangle$ is the ensemble average of the particle velocity taken over one potential period [5]. For our simple initialization condition, i.e., $g(E_i) = (1-\alpha)\delta(E_i) + \alpha\delta(E_i - E_\alpha)$, from the identity $\langle |\bar{v}| \rangle = \alpha|\bar{v}(E_\alpha)|$ it follows immediately that $D = \alpha|\bar{v}(E_\alpha)|/(2\rho)$. In Fig. 1(d) our prediction has been tested by plotting the ratio $\langle \Delta x^2(t) \rangle / |\bar{v}(E_\alpha)|$ versus t for different E_α and constant α and ρ: all curves tend to collapse on one asymptotic scaling function $\alpha t/(2\rho)$.

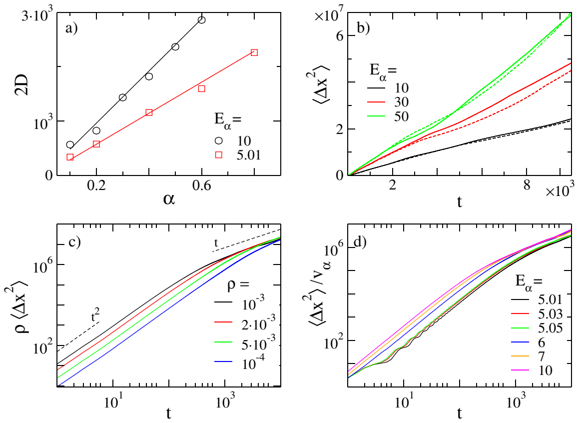

FIG. 1 (color online). Diffusion of a BSF in the periodic potential (4): (a) diffusion coefficient D vs α for $\rho = 10^{-3}$ and different energies E_α. The solid curves represent the equality $2D = \langle |\bar{v}| \rangle/\rho$ introduced in Eq. (5); note that the BSF diffusion law sets in only for relatively large running times, i.e., $t(\rho\langle|\bar{v}|\rangle) \gg 1$, as shown in (c) and (d); (b) $\langle \Delta x^2(t) \rangle$ vs t for $\alpha = 0.6$ and different SF initializations. Solid curves: all αN running particles are given the same energy E_α; dashed curves: the initial energy of the running particles is distributed according to a Gaussian function with mean E_α and variance $(E_\alpha - 2d)/3$, while the energy of the trapped particles is set to zero. Choosing (random) positive values for the energies of the trapped particles does not affect the long-time diffusion process (not shown); (c) $\langle \Delta x^2(t) \rangle$ vs t for $\alpha = 0.6$, $E_\alpha = 10$, and different densities ρ. The t^2 and the t slopes (dashed lines) have been drawn for reader's convenience; (d) numerical test of the diffusion law (5) (see text) for $\alpha = 0.6$, $\rho = 10^{-3}$, and different values of E_α. The factor $v_\alpha \equiv |\bar{v}(E_\alpha)|$ has been computed as in Ref. [5], Eq. (11.102). Other simulation parameters are $L = 1.5 \times 10^6$, $l = 10^3$, $d = 5$, and all particles have unit mass. The mean square displacement $\langle \Delta x^2(t) \rangle$ of a BSF is defined as $\frac{1}{N} \times \sum_{i=1}^{N}[x_i(t) - x_i(0)]^2$, where x_i is the coordinate of the ith particle. To improve our statistics, averages have been taken over 5 independent realizations.

The diffusion law (5) can be interpreted as follows. Over time, each SF particle visits all N individual (i.e., collisionless) particle trajectories uniquely determined by the initial conditions. One such trajectory with energy E can be either open or closed, but it sure is periodic—the average velocity $|\bar{v}(E)|$ is zero for the trapped particles and grows from $(4/\pi)\sqrt{d}$ up to $\sqrt{2E}$ with E larger than $2d$ [5]. The residence time τ of a tagged particle in any trajectory is the time interval between two subsequent collisions, that is, on average, $\tau = (\rho\langle|\bar{v}|\rangle)^{-1}$. On regarding such N trajectories as a statistical ensemble of distinct microscopic states, we conclude that a tagged particle behaves like a random walker that executes jumps of length $\pm 1/\rho$ sidewise at average time intervals τ; hence, Einstein's diffusion constant $D = \langle |\bar{v}| \rangle / 2\rho$ in Eq. (5).

The interpretation of the identity $D = \alpha |\bar{v}(E_\alpha)|/(2\rho)$ is quite intriguing. Consider our simulation model, where E_i assumes only two values, 0 and E_α, with probability $1 - \alpha$ and α, respectively: how can an experimenter determine the SF density? On measuring D, as it was originally proposed by Einstein, one extracts an estimate for ρ/α. However, this ratio can be kept constant by increasing ρ and simultaneously lowering d (i.e., raising α). Moreover, note that ρ/α can be regarded as the particle density of a free SF confined to the length αL covered on average by the running particles. This is an effect of the potential wells trapping a fraction $1 - \alpha$ of the particles with zero mean velocity (closed orbits): the kinetic energy of the trapped particles, no matter what the particle initialization, does not contribute to the overall BSF diffusion.

Stochastic single file.—The simulation of a SSF in the sinusoidal potential (4) requires assigning each particle an independent Brownian dynamics determined by a viscous force $-\eta \dot{x}_i$ and a random force $\xi_i(t)$. Here, $x_i(t)$ denotes the coordinate of the ith particle; $\xi_i(t)$ represents a Gaussian stochastic process with zero mean and autocorrelation function $\langle \xi_i(t) \xi_j(0) \rangle = 2\eta kT \delta_{i,j} \delta(t)$. Such a coupling of the diffusing particles with their environment ensures that the SF eventually approaches an equilibrium state with temperature T, both in the underdamped, $\eta \ll (2\pi/l)\sqrt{d}$, and in the overdamped regime, $\eta \gg (2\pi/l)\sqrt{d}$.

The outcome of our numerics led us to conclude that the periodic substrate potential $V(x)$ does not invalidate the SSF diffusion law (3), although the dependence of the mobility factor F on the system parameters becomes more complicated. In Figs. 2(a)–2(c) we characterize F as a function of η, d, and T. The identity $F = \sqrt{D_0/\pi}$ assumed in Eq. (3) for $V(x) \equiv 0$ seems to apply here, too. In 2(a) the rescaled curves $\eta^{1/2}\langle \Delta x^2(t) \rangle$ versus t overlap asymptotically for any damping regime. The temperature dependence of the factor F is more interesting. In the regime of moderate-to-large damping the diffusive dynamics of a single Brownian particle can be modeled as a renewal process [17,24] with modified diffusion constant

$$D_0 = \frac{l^2 kT}{\eta} \frac{\int_0^l dx I_+^2(x) I_-(x)}{[\int_0^l dx I_+(x)]^3}, \qquad (6)$$

where $I_\pm(x) = \int_0^l dy \exp\{[\pm V(x) \mp V(x \mp y) - yA]/kT\}$ with $A = 0$. This prediction is known to get more and more accurate for large η [16] and increasingly high activation-to-thermal energy ratios d/T [17]. In view of Eq. (6) the rescaled mobility $\sqrt{\eta/d} F$ would be a function of d/T, alone, in good agreement with the simulation results displayed in 2(c). Note that our analytical prediction based on Cox's theory (solid curve) fits quantitatively well the numerical data for a wide parameter range.

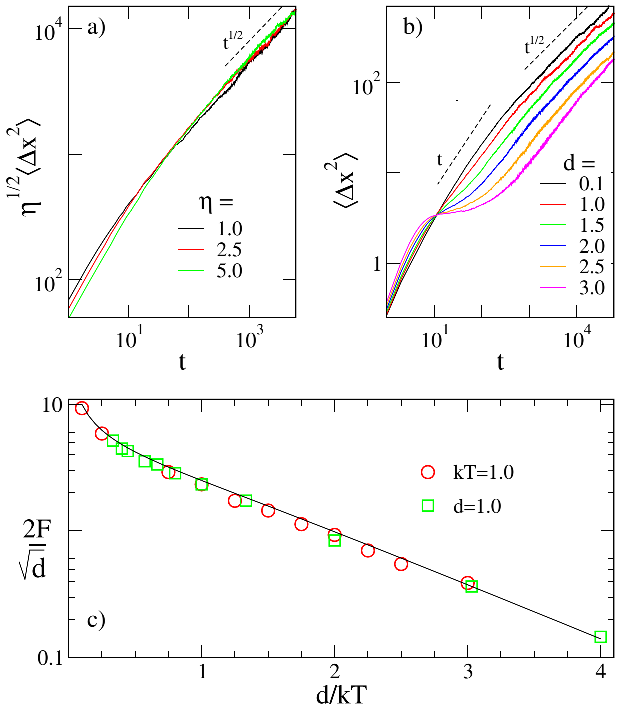

FIG. 2 (color online). Diffusion of a SSF in the periodic potential (4): (a) $\langle \Delta x^2(t) \rangle$ vs t for $kT = 1$, $d = 1$, and different η; (b) $\langle \Delta x^2(t) \rangle$ vs t for $kT = 1$, $\eta = 5$, and different d. The t and the $t^{1/2}$ slopes (dashed lines) have been drawn for the reader's convenience; (c) the mobility factor F vs d/kT for $\eta = 5$ and $d = 1$ (circles) and $kT = 1$ (squares). The solid curve in (c) represents the law $F = \sqrt{D_0/\pi}$ with D_0 given by Eq. (6) with $A = 0$. Moreover, our simulation confirms that $\langle \Delta x^2(t) \rangle$ is inverse proportional to ρ in the range $[10^2, 1]$ (not shown). Other simulation parameters are $N = 3 \times 10^3$, $l = 2\pi$, $L = 3 \times 10^3 l$, and all particles have unit mass. Here, the definition of the SSF mean square displacement is $\langle \Delta x^2(t) \rangle = \frac{1}{N}\sum_{i=1}^N \langle [x_i(t) - x_i(0)]^2 \rangle_s$, with $\langle \cdots \rangle_s$ denoting the average taken over 5 independent stochastic realizations. Note that in (b) $\langle \Delta x^2(t) \rangle$ for $d \gg kT$ approaches first $\langle x^2(0) \rangle = \pi^2/3$ [uniform $x_i(0)$ distribution] on the short time scale η/d, before the diffusive hopping dynamics sets in.

Such a close comparison between theory and simulation encouraged us to explore the case of file diffusion in the presence of a nonvanishing external tilt A; namely, we now assume that all file particles are subjected to an additional constant force A pointing, say, to the right ($A \geq 0$). [Of course, because of the absence of a damping term, a driven BSF is out of the question.] The diffusion of a single Brownian particle drifting down a tilted washboard potential is known to exhibit enhanced normal diffusion [16] with diffusion constant (6) [17]. Extensive simulation of a driven SSF yielded the numerical data reported in Fig. 3. In both damping regimes the kinetic mobility of the file, defined as $\mu \equiv \langle \dot{x} \rangle / A$, is expected to coincide with the mobility of a single particle under the same dynamical conditions [13] (Fig. 3, inset).

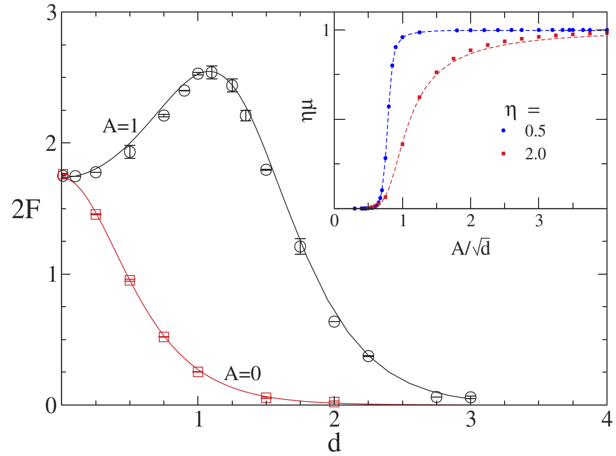

FIG. 3 (color online). Diffusion of a SSF in the periodic potential (4): the mobility factor F vs d for $kT = 0.3$, $\eta = 5$, and $A = 0$ (squares) and $A = 1$ (circles). The solid curves represent the law $F = \sqrt{D_0/\pi}$ with D_0 given by Eq. (6). Other simulation details are as in Fig. 2. Inset: the kinetic mobility, $\mu \equiv \langle \dot{x} \rangle / A$, vs $A/\sqrt{d}$ for $\eta = 0.5$ (circles) and $\eta = 2$ (squares) at $kT = 0.1$. The fitting curves are the corresponding analytical predictions for a single Brownian particle based, respectively, on Eqs. (11.194) and (11.50) of Ref. [5].

More remarkably, the SF diffusion regime persists, though with an A-dependent mobility factor; when plotted versus d, F attains a maximum enhancement for $d \gtrsim A$, i.e., in coincidence with the (noise-assisted) depinning of the file from its sinusoidal substrate [16]. Again, the identity $F = \sqrt{D_0/\pi}$ combined with Cox's formula (6) provides an excellent fit of our simulation data for large η. Of course, the mobility enhancement at depinning can be revealed also by plotting F versus A at constant d.

In conclusion, we have generalized the most refined SF diffusion laws (2) and (3) to BSF and SSF on periodic substrates. The diffusion coefficients D and F, respectively, can be modified analytically to closely reproduce the numerical results from stochastic molecular dynamics simulations. Most remarkably, we extended our analysis to the case of driven SSF: a marked enhancement of the mobility factor F versus A at different T, can allow an experimentalist to determine the file depinning threshold, i.e., the substrate amplitude, with good accuracy. Finally, the SSF diffusion properties illustrated here are expected to apply also when the stochastic particle dynamics is replaced by a chaotic one, as is the case of the narrow corrugated channels investigated in Ref. [18].

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