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Intrinsic friction of adsorbed monolayers

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Abstract

In the present paper we overview our recent results on intrinsic frictional properties of adsorbed monolayers, composed of mobile hard-core particles undergoing continuous exchanges with a vapour phase. Within the framework of a dynamical master equation approach, describing the time evolution of the system, we determine in the most general form the terminal velocity of some biased impure molecule—the tracer particle (TP), constrained to move inside the adsorbed monolayer, probing its frictional properties—and define the frictional forces as well as the particle-density distribution in the monolayer. Results for one-dimensional solid substrates, appropriate to adsorption on polymer chains, are compared against the Monte Carlo simulation data, which confirm our analytical predictions.

1. Introduction

In the present paper we overview our recent results on intrinsic friction of monolayers emerging on solids exposed to a vapour phase [1–4]. Such layers are involved in various technological and materials processing operations, including, for instance, coating, gluing and lubrication. Knowledge of their intrinsic frictional properties is important for a conceptual understanding of different transport processes taking place within molecular films, film stability, as well as the spreading of ultrathin liquid films on solid surfaces [5, 6], spontaneous or forced dewetting of monolayers [7–10] and island formation on solid surfaces [11].

Since the early works of Langmuir, much effort has been invested in the analysis of the equilibrium properties of adsorbed films [12–16]. Here, significant analytical results have been obtained predicting different phase transitions and ordering phenomena, which agree well with the available experimental data. Also, some approximate results have been obtained for both the dynamics of an isolated adatom on a corrugated surface and collective diffusion, describing spreading of the macroscopic density fluctuations in interacting adsorbates that are in contact with the vapour [17–20].

Another important aspect of the dynamical behaviour concerns tracer diffusion in adsorbates, which is observed experimentally in STM or field-ion measurements and provides

useful information about an adsorbate's viscosity or intrinsic friction. This problem is not only a challenging question in its own right due to emerging non-trivial, essentially cooperative behaviour, but is also crucial for the understanding of various dynamical processes taking place on solid surfaces. However, most of the available theoretical studies of tracer diffusion in adsorbed layers (see, e.g., references [21–29]) exclude the possibility of particle exchanges with the vapour.

Here we focus on this important issue and provide a theoretical description of the properties of tracer diffusion in adsorbed monolayers in contact with a vapour phase—a reservoir of particles. More specifically, the system that we consider consists of (a) a solid substrate, which is modelled in the usual fashion as a regular lattice of adsorption sites; (b) a monolayer of adsorbed, mobile hard-core particles in contact with a vapour; and (c) a single hard-core tracer particle (TP). We suppose that the monolayer particles move randomly through the lattice by performing symmetric hopping motions between the neighbouring lattice sites—which process is constrained by mutual hard-core interactions—and may desorb from and adsorb onto the lattice from the vapour with some prescribed rates dependent on the vapour pressure, temperature and the interactions with the solid substrate. In contrast, the tracer particle is constrained to move through the lattice only (i.e. it cannot desorb to the vapour), and is subject to a constant external force of arbitrary magnitude E . Hence, the TP performs a biased random walk, constrained by the hard-core interactions with the monolayer particles, and always remains within the monolayer, probing its frictional properties.

The questions that we address here are the following. First, focusing on one- and two-dimensional systems, we aim to determine the force–velocity relation. That is, as $t \rightarrow \infty$, the TP ultimately attains a constant velocity $V_{tr}(E)$, which depends on the magnitude of the applied external force; the functional form of this dependence in the most general case constitutes the primary goal of our analysis. Next, we study the form of the force–velocity relation in the limit of a vanishingly small external bias. This allows us, in particular, to show that the frictional force exerted on the TP by the monolayer particles is viscous, and to evaluate the corresponding friction coefficient. Lastly, we analyse how the biased TP perturbs the particle-density distribution in the monolayer. In fact, we proceed to show that there are stationary density profiles around the TP as $t \rightarrow \infty$, which mirror a remarkable cooperative behaviour.

We finally remark that our model can be viewed from a somewhat different perspective. Namely, on the one hand, the model under study is a certain generalization of the ‘tracer diffusion in a hard-core lattice gas’ problem (see, e.g., reference [21] for an extensive review) to the case where the random walk performed by the TP is *biased* and the number of particles in the monolayer is *not explicitly conserved*, due to exchanges with the reservoir. We recall that even this, by now classic model constitutes a many-body problem for which no exact general expression for the tracer diffusion coefficient D_{tr} is known. On the other hand, our model represents a novel example of the so-called ‘dynamical percolation’ models [30–35], invoked to describe transport processes in many situations with dynamical disorder. In this context, the particles of the monolayer can be thought of as representing some fluctuating environment, which hinders the motion of an impure molecule—the TP, which might be, for example, a charge carrier. An important aspect of our model, which makes it different from the previously proposed models of dynamic percolative environments, is that we include the hard-core interaction between ‘environment’ particles and the tracer particle, such that the latter may itself influence the dynamics of the environment. Lastly, we note that the model under study can be thought of as some simplified picture of the stagnant layers emerging in liquids that are in contact with a solid body. It is well known (see, e.g., reference [36]) that liquids in the close vicinity of a solid interface—at distances within a few molecular diameters—do possess completely different physical properties compared to those of the bulk phase. In

this ‘stagnant’ region, in which an intrinsically disordered liquid phase is spanned by and interacts with the ordering potential of the solid, the liquid’s viscosity is drastically enhanced and transport processes (related, say, to biased diffusion of charged carriers in solutions) are substantially hindered. Thus our model can be viewed as a two-level approximate model of this challenging physical system, in which the reservoir mimics the bulk fluid phase with very rapid transport, while the adsorbed monolayer represents the stagnant layer emerging on the solid–liquid interface.

The paper is structured as follows. In section 2 we formulate our model for the case of a two-dimensional solid substrate and introduce the basic notation. We then write down the dynamical equations which govern the time evolution of the monolayer particles and of the tracer, and outline the decoupling approximation used to close this system of equations. These equations are presented for the general, d -dimensional case. Sections 3 and 4 are respectively devoted to the presentation of the results of this general approach for one-dimensional substrates—which situation is appropriate to adsorption on polymer chains [37,38]—and also for two-dimensional solid substrates. Finally, we conclude in section 5 with a brief summary and a discussion of our results.

2. The model and basic equations

2.1. The model

Consider a two-dimensional solid surface with some concentration of adsorption sites, which is brought in contact with a reservoir containing identical, electrically neutral particles—a vapour phase (figure 1), maintained at a constant pressure. For simplicity of exposition, we assume here that adsorption sites form a regular square lattice of spacing σ . We suppose next that the reservoir particles may adsorb onto any vacant adsorption site at a fixed rate f/τ^* , which rate depends on the vapour pressure and the energy gain due to the adsorption event. Further on, the adsorbed particles may move randomly through the lattice by hopping at a rate $1/4\tau^*$ to any of four neighbouring adsorption sites, which process is constrained by hard-core

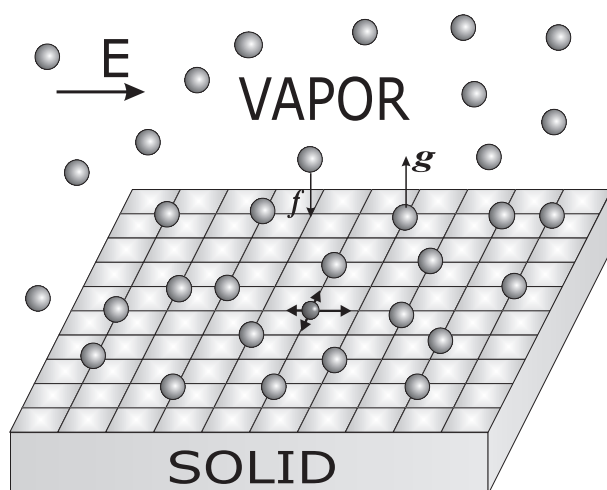


Figure 1. An adsorbed monolayer in contact with a vapour. Grey spheres denote the monolayer (vapour) particles; the smaller dark sphere stands for the driven tracer particle.

exclusion preventing multiple occupancy of any of the sites. Lastly, the adsorbed particles may desorb from the lattice back to the reservoir at the rate g/τ^* , which is dependent on the barrier against desorption. Both f and g are site and environment independent.

Note that such a model represents, of course, a certain idealization. In ‘real-world’ systems, the adsorbed particles experience two types of interaction: the solid–particle (SP) interactions, i.e. interactions with the atoms of the host solid, and the particle–particle (PP) interactions, i.e. mutual interactions with each other. Now, both the SP and the PP interactions are characterized by a strong repulsion at short distances, and are attractive at longer distances. The SP repulsion keeps the adsorbed particles some distance apart from the solid, while the SP attraction favours adsorption and hinders particle desorption as well as migration along the solid surface. In this regard, our model corresponds to the regime of the so-called intermediate localized adsorption [15, 16]: the particles forming an adsorbed monolayer are neither completely fixed in the potential wells created by the SP interactions, nor completely mobile. This means that the potential wells are rather deep with respect to particle desorption (the desorption barrier $U_d \gg kT$), such that the adsorbate forms a submonolayer, but nonetheless, have a much lower energy barrier V_l against the lateral movement across the surface, $U_d \gg V_l > kT$. In this regime, each adsorbed particle spends a considerable part of its time at the bottom of a potential well and jumps sometimes, solely due to the thermal activation, from one potential minimum to another in its neighbourhood; after the jump is performed, the particle dissipates all of its energy to the host solid. Thus, on a macroscopic timescale the particles do not possess any velocity. The time τ^* separating two successive jump events is just the typical time that a given particle spends in a given well vibrating around its minimum; τ^* is related to the temperature, the barrier for lateral motion and the frequency of the solid atoms’ vibrations by the Arrhenius formula.

We emphasize that such random motion is essentially different from the standard hydrodynamic picture of particle random motion in the two-dimensional ‘bulk’ liquid phase, e.g. in free-standing liquid films, in which case there is a velocity distribution and spatially *random* motion results from the PP scattering. In this case, the dynamics may be only approximately considered as an activated hopping of particles, confined to some effective cells by the potential field of their neighbours, through a lattice-like structure of such cells (see, e.g., references [39, 40]). In contrast to the dynamical model to be studied here, standard two-dimensional hydrodynamics presumes that the particles do not interact with the underlying solid. In real systems, of course, both the particle–particle scattering and the scattering by the potential wells due to the interactions with the host solid (as well as the corresponding dissipation channels) are important [18, 41]. In particular, it has been shown that addition of a dissipation to the host solid removes the infrared divergencies in the dynamic density correlation functions and thus makes the transport coefficients finite [42, 43]. On the other hand, homogeneous adsorbed monolayers may only exist in systems in which the attractive part of the PP interaction potential is essentially weaker than that describing interactions with the solid; otherwise, such monolayers become unstable and dewet spontaneously from the solid surface. In fact, for stable homogeneous monolayers, the PP interactions are at least ten times weaker than the interactions with the solid atoms [16].

Consequently, the standard hydrodynamic picture of particle dynamics is inappropriate under the above-defined physical conditions. On the contrary, any adsorbed particle moves due to random hopping events, activated by chaotic vibrations of the solid atoms, through the local minima of an array of potential wells, created due to the interactions with the solid [15, 16]. As we have already remarked, in the physical conditions under which such a dynamics occurs, the PP interactions are much weaker than the SP interactions and hence do not significantly perturb the regular array of potential wells due to the SP interactions. In our model, we completely

discard the attractive part of the PP interaction potential and take into account only the repulsive one, which is approximated by an abrupt, hard-core-type potential.

To describe the occupancy of lattice sites, we introduce a time-dependent variable $\eta(\mathbf{R})$, which may assume either of two values:

$$\eta(\mathbf{R}) = \begin{cases} 1 & \text{if the site } \mathbf{R} \text{ is occupied by an adsorbed particle} \\ 0 & \text{if the site } \mathbf{R} \text{ is empty.} \end{cases} \quad (1)$$

Note that the local variable $\eta(\mathbf{R})$ can change its value due to adsorption, desorption and random hopping events. Note also that random hopping events conserve the total number of adsorbed particles and, hence, also the average adsorbate density $\rho_s(t)$. On the other hand, adsorption/desorption processes change $\eta(\mathbf{R})$ locally such that the total number of particles in the adsorbed monolayer is not explicitly conserved. However, the mean density of the adsorbate, $\rho_s(t) = \langle \eta(\mathbf{R}) \rangle$, approaches as $t \rightarrow \infty$ a constant value:

$$\rho_s = \frac{f}{f + g}. \quad (2)$$

This relation is well known and represents the customary Langmuir adsorption isotherm [12]. We finally remark that in the analysis of the stationary-state behaviour, we can always turn to the conserved-particle-number limit by setting f and g equal to zero and keeping their ratio fixed, i.e. supposing that $f/g = \rho_s/(1 - \rho_s)$. This limit will correspond to the model of biased tracer diffusion in a hard-core lattice gas with fixed particle density ρ_s , and will allow us to check our analytical predictions against some already known results [21–25, 29]. We will furnish such a comparison at the end of the section 4.

Further on, at $t = 0$ we introduce at the lattice origin an extra hard-core particle, whose motion we would like to follow; the position of this particle at time t is denoted as \mathbf{R}_{tr} . Note that the tracer particle (TP) is designed to measure the resistance offered by the monolayer particles to the external perturbation, or, in other words, to measure the intrinsic frictional properties of the adsorbate.

Now, we stipulate that the TP is different from the adsorbed particles in two respects: first, it cannot desorb from the lattice and second, it is subject to some external driving force, which favours jumps in a preferential direction. Physically, such a situation may be realized, for instance, if only this particle is charged and the system is subject to a uniform electric field \mathbf{E} . We suppose here, for simplicity of exposition, that the external force \mathbf{E} is oriented according to the unit vector \mathbf{e}_1 .

The dynamics of the biased TP is defined in the usual fashion: we suppose that the TP, which occupies the site \mathbf{R}_{tr} at time t , waits an exponentially distributed time with mean τ , and then attempts to hop onto one of four neighbouring sites, $\mathbf{R}_{tr} + \mathbf{e}_\nu$, where the \mathbf{e}_ν are the four unit vectors of the hypercubic lattice. In what follows, we adopt the notation $\nu = \{\pm 1, \pm 2\}$; $\pm \mathbf{e}_1$ will denote the direction of the external force \mathbf{E} . Next, the jump direction is chosen according to the probability p_ν , which obeys

$$p_\nu = \exp\left[\frac{\beta}{2}(\mathbf{E} \cdot \mathbf{e}_\nu)\right] / \sum_{\mu} \exp\left[\frac{\beta}{2}(\mathbf{E} \cdot \mathbf{e}_\mu)\right] \quad (3)$$

where β is the reciprocal temperature, $(\mathbf{E} \cdot \mathbf{e})$ stands for the scalar product, the charge of the TP is set equal to unity and the sum with the subscript μ denotes summation over all possible orientations of the vector \mathbf{e}_μ ; that is, $\mu = \{\pm 1, \pm 2\}$.

After the jump direction is chosen, the TP attempts to hop onto the target site. The hop is instantaneously effected if the target site is vacant at this moment of time; otherwise, i.e. if the target site is occupied by any adsorbed particle, the jump is rejected and the TP remains at its position.

2.2. Evolution equations

Now, we derive the evolution equations in a general, d -dimensional case, which will allow us to compare the behaviour emerging in one- and two-dimensional systems. We begin by introducing some auxiliary definitions. Let $\eta \equiv \{\eta(\mathbf{R})\}$ denote the entire set of the occupation variables, which defines the instantaneous configuration of the adsorbed particles at the lattice at moment t . Next, let $P(\mathbf{R}_{tr}, \eta; t)$ stand for the joint probability of finding at time t the TP at the site \mathbf{R}_{tr} and all adsorbed particles in the configuration η . Then, denoting as $\eta^{r,\nu}$ a configuration obtained from η by the Kawasaki-type exchange of the occupation variables of two neighbouring sites r and $r + e_\nu$, and as $\hat{\eta}^r$ a configuration obtained from the original η by the replacement $\eta(r) \rightarrow 1 - \eta(r)$, which corresponds to the Glauber-type flip of the occupation variable due to the adsorption/desorption events, we have that the time evolution of the configuration probability $P(\mathbf{R}_{tr}, \eta; t)$ obeys the following master equation:

$$\begin{aligned} \partial_t P(\mathbf{R}_{tr}, \eta; t) = & \frac{1}{2d\tau^*} \sum_{\mu=1}^d \sum_{r \neq \mathbf{R}_{tr} - e_\mu, \mathbf{R}_{tr}} \{P(\mathbf{R}_{tr}, \eta^{r,\mu}; t) - P(\mathbf{R}_{tr}, \eta; t)\} \\ & + \frac{1}{\tau} \sum_{\mu} p_\mu \{(1 - \eta(\mathbf{R}_{tr}))P(\mathbf{R}_{tr} - e_\mu, \eta; t) \\ & - (1 - \eta(\mathbf{R}_{tr} + e_\mu))P(\mathbf{R}_{tr}, \eta; t)\} \\ & + \frac{g}{\tau^*} \sum_{r \neq \mathbf{R}_{tr}} \{(1 - \eta(r))P(\mathbf{R}_{tr}, \hat{\eta}^r; t) - \eta(r)P(\mathbf{R}_{tr}, \eta; t)\} \\ & + \frac{f}{\tau^*} \sum_{r \neq \mathbf{R}_{tr}} \{\eta(r)P(\mathbf{R}_{tr}, \hat{\eta}^r; t) - (1 - \eta(r))P(\mathbf{R}_{tr}, \eta; t)\}. \end{aligned} \quad (4)$$

The mean velocity $V_{tr}(t)$ of the TP can be obtained by multiplying both sides of equation (4) by $(\mathbf{R}_{tr} \cdot \mathbf{e}_1)$ and summing over all possible configurations (\mathbf{R}_{tr}, η) . This results in the following exact equation determining the TP velocity:

$$V_{tr}(t) \equiv \frac{d}{dt} \sum_{\mathbf{R}_{tr}, \eta} (\mathbf{R}_{tr} \cdot \mathbf{e}_1) P(\mathbf{R}_{tr}, \eta; t) = \frac{\sigma}{\tau} \{p_1(1 - k(\mathbf{e}_1; t)) - p_{-1}(1 - k(\mathbf{e}_{-1}; t))\} \quad (5)$$

where

$$k(\boldsymbol{\lambda}; t) \equiv \sum_{\mathbf{R}_{tr}, \eta} \eta(\mathbf{R}_{tr} + \boldsymbol{\lambda}) P(\mathbf{R}_{tr}, \eta; t) \quad (6)$$

is the probability of having at time t an adsorbed particle at position $\boldsymbol{\lambda}$, defined in the frame of reference moving with the TP. In other words, $k(\boldsymbol{\lambda}; t)$ can be thought of as being the density profile in the adsorbed monolayer as seen from the moving TP.

Equation (5) signifies that the velocity of the TP is dependent on the monolayer particle density in the immediate vicinity of the tracer. If the monolayer is perfectly stirred, or, in other words, if $k(\boldsymbol{\lambda}; t) = \rho_s$ everywhere (which implies immediate decoupling of \mathbf{R}_{tr} and η), one would obtain from equation (5) a trivial mean-field result:

$$V_{tr}^{(0)} = (p_1 - p_{-1})(1 - \rho_s) \frac{\sigma}{\tau} \quad (7)$$

which states that the only effect of the medium on the TP dynamics is that its jump time τ is merely renormalized by a factor $(1 - \rho_s)^{-1}$, which represents the inverse concentration of voids in the monolayer; note that then $(1 - \rho_s)/\tau$ defines simply the mean frequency of successful jump events.

However, the situation appears to be more complicated and, as we proceed to show, $k(\boldsymbol{\lambda}; t)$ is different from the equilibrium value ρ_s everywhere, except for when $|\boldsymbol{\lambda}| \rightarrow \infty$. This means

that the TP strongly perturbs the particle distribution in the monolayer—it is no longer uniform and some non-trivial stationary density profiles emerge.

Now, in order to calculate the instantaneous mean velocity of the TP we have to determine the mean particle density at the sites neighbouring the TP, $\mathbf{R}_{tr} + \mathbf{e}_{\pm 1}$, which requires, in turn, computation of the density profile $k(\boldsymbol{\lambda}; t)$ for arbitrary $\boldsymbol{\lambda}$. The latter can be found from the master equation (4) by multiplying both sides by $\eta(\mathbf{R}_{tr})$ and performing the summation over all configurations (\mathbf{R}_{tr}, η) . In doing so, we find that these equations are not closed with respect to $k(\boldsymbol{\lambda}; t)$, but are coupled to the third-order correlations:

$$T(\boldsymbol{\lambda}, \mathbf{e}_v; t) = \sum_{\mathbf{R}_{tr}, \eta} \eta(\mathbf{R}_{tr} + \boldsymbol{\lambda}) \eta(\mathbf{R}_{tr} + \mathbf{e}_\mu) P(\mathbf{R}_{tr}, \eta; t). \quad (8)$$

In turn, if we proceed further to the third-order correlations, we find that these are coupled respectively to the fourth-order correlations. Consequently, in order to compute V_{tr} , one faces the problem of solving an infinite hierarchy of coupled equations for the correlation functions. Here we resort to the simplest non-trivial closure of the hierarchy in terms of $k(\boldsymbol{\lambda}; t)$, which was first proposed in references [26] and [27], and represent $T(\boldsymbol{\lambda}, \mathbf{e}_v; t)$ as

$$\begin{aligned} & \sum_{\mathbf{R}_{tr}, \eta} \eta(\mathbf{R}_{tr} + \boldsymbol{\lambda}) \eta(\mathbf{R}_{tr} + \mathbf{e}_\mu) P(\mathbf{R}_{tr}, \eta; t) \\ & \approx \left(\sum_{\mathbf{R}_{tr}, \eta} \eta(\mathbf{R}_{tr} + \boldsymbol{\lambda}) P(\mathbf{R}_{tr}, \eta; t) \right) \left(\sum_{\mathbf{R}_{tr}, \eta} \eta(\mathbf{R}_{tr} + \mathbf{e}_\mu) P(\mathbf{R}_{tr}, \eta; t) \right) \\ & = k(\boldsymbol{\lambda}; t) k(\mathbf{e}_\mu; t). \end{aligned} \quad (9)$$

Some arguments justifying such an approximation *a posteriori* are presented in sections 3 and 4 (see also reference [1]).

Using the approximation in equation (9), we obtain

$$2d\tau^* \partial_t k(\boldsymbol{\lambda}; t) = \tilde{L}k(\boldsymbol{\lambda}; t) + 2df \quad (10)$$

which holds for all $\boldsymbol{\lambda}$, except for $\boldsymbol{\lambda} = \{\mathbf{0}, \pm \mathbf{e}_1, \mathbf{e}_2, \dots, \mathbf{e}_d\}$. On the other hand, for these special sites $\boldsymbol{\lambda} = \mathbf{e}_v$ with $v = \{\pm 1, 2, \dots, d\}$ we find

$$2d\tau^* \partial_t k(\mathbf{e}_v; t) = (\tilde{L} + A_v)k(\mathbf{e}_v; t) + 4f \quad (11)$$

where \tilde{L} is the operator

$$\tilde{L} \equiv \sum_{\mu} A_{\mu} \nabla_{\mu} - 4(f + g). \quad (12)$$

∇_{μ} is defined by its action over test functions $f(\boldsymbol{\lambda})$ by

$$\nabla_{\mu} f(\boldsymbol{\lambda}) \equiv f(\boldsymbol{\lambda} + \mathbf{e}_{\mu}) - f(\boldsymbol{\lambda}) \quad (13)$$

and the coefficients A_{μ} are the following quantities:

$$A_{\mu}(t) \equiv 1 + \frac{2d\tau^*}{\tau} p_{\mu}(1 - k(\mathbf{e}_{\mu}; t)). \quad (14)$$

Note that equation (11) represents, from the mathematical point of view, the boundary conditions for the general evolution equation (10), imposed on the sites in the immediate vicinity of the TP. Equations (10) and (11) together with equation (5) thus constitute a closed system of equations which suffice for computation of all properties of interest.

2.3. Stationary solution of the evolution equations

We turn to the limit $t \rightarrow \infty$ and suppose that both the density profiles and stationary velocity of the TP have non-trivial stationary values:

$$k(\lambda) \equiv \lim_{t \rightarrow \infty} k(\lambda; t) \quad V_{tr} \equiv \lim_{t \rightarrow \infty} V_{tr}(t) \quad A_\mu \equiv \lim_{t \rightarrow \infty} A_\mu(t). \quad (15)$$

Define next the local deviations of $k(\lambda)$ from the unperturbed density as

$$h(\lambda) \equiv k(\lambda) - \rho_s. \quad (16)$$

Choosing that $h(\mathbf{0}) = 0$, we obtain then the following fundamental system of equations:

$$\tilde{L}h(\lambda) = 0 \quad \text{for all } \lambda \neq \{\mathbf{0}, e_{\pm 1}, \dots, e_{\pm d}\} \quad (17)$$

$$(\tilde{L} + A_\nu)h(e_\nu) + \rho_s(A_\nu - A_{-\nu}) = 0 \quad \text{for } \lambda = \{\mathbf{0}, e_{\pm 1}, \dots, e_{\pm d}\} \quad (18)$$

which determine the deviation from the unperturbed density ρ_s in the stationary state. Note also that by virtue of an evident symmetry, $h(e_\nu) = h(e_{-\nu})$ and $A_\nu = A_{-\nu}$ for $\nu \in \{2, \dots, d\}$.

The general approach to the solution of the coupled non-linear equations (5), (17) and (18) has been discussed in detail in reference [4]. Here we merely note that despite the fact that using the decoupling scheme in equation (9) we effectively close the system of equations on the level of the pair correlations, solution of equations (17) and (18) (or, equivalently, of equations (10) and (11)) still poses serious technical difficulties: namely, these equations are non-linear with respect to the TP velocity, which enters the gradient term on the rhs of the evolution equations for the pair correlation, and itself depends on the values of the monolayer particle densities in the immediate vicinity of the TP. The solution of this system of non-linear equations for one- and two-dimensional substrates is demonstrated in the next two sections.

3. One-dimensional adsorbed monolayer

For one-dimensional lattices, which situation is appropriate to adsorption on polymer chains [37, 38], the general solution of equations (17) and (18) has the following form:

$$k_n \equiv k(\lambda) = \rho_s + K_\pm \exp(-\sigma|n|/\lambda_\pm) \quad \lambda = \sigma n \quad n \in \mathbb{Z}^* \quad (19)$$

where the characteristic lengths λ_\pm obey

$$\lambda_\pm = \mp \sigma \ln^{-1} \left[\frac{A_1 + A_{-1} + 2(f+g) \mp \sqrt{(A_1 + A_{-1} + 2(f+g))^2 - 4A_1A_{-1}}}{2A_1} \right] \quad (20)$$

while the amplitudes K_\pm are given respectively by

$$K_+ = \rho_s \frac{A_1 - A_{-1}}{A_{-1} - A_1 \exp(-\sigma/\lambda_+)} \quad (21)$$

and

$$K_- = \rho_s \frac{A_1 - A_{-1}}{A_{-1} \exp(-\sigma/\lambda_-) - A_1}. \quad (22)$$

Note that $\lambda_- > \lambda_+$ and, consequently, the local density past the TP approaches its non-perturbed value ρ_s more slowly than that in front of it; this signifies that correlations between the TP position and particle distribution are stronger past the TP. Next, K_+ is always positive, while $K_- < 0$; this means that the density profile is a non-monotonic function of λ and is characterized by a jammed region in front of the TP, in which the local density is higher than ρ_s , and a depleted region past the TP in which the density is lower than ρ_s .

Now, we are in position to obtain a system of two closed-form non-linear equations determining implicitly the unknown parameters A_1 and A_{-1} , which will allow us to compute the TP terminal velocity, related to $A_{\pm 1}$ through $V_{tr} = \sigma(A_1 - A_{-1})/2\tau^*$. Substituting equation (19) into equation (14), we find

$$A_1 = 1 + \frac{p_1 \tau^*}{\tau} \left[1 - \rho_s - \rho_s \frac{A_1 - A_{-1}}{A_{-1} \exp(\sigma/\lambda'_+) - A_1} \right] \quad (23)$$

and

$$A_{-1} = 1 + \frac{p_{-1} \tau^*}{\tau} \left[1 - \rho_s - \rho_s \frac{A_1 - A_{-1}}{A_{-1} - A_1 \exp(\sigma/\lambda'_-)} \right]. \quad (24)$$

Resolution of this system leads then to the stationary velocity of the TP (see figure 2) as well as the density profiles (see figure 3). For arbitrary values of p , f and g , the parameters $A_{\pm 1}$, defined by equations (23) and (24), and, consequently, the terminal velocity V_{tr} can be determined only numerically (see figures 2 to 4). However, V_{tr} can be found analytically in an explicit form in the limit of a vanishingly small force E , $E \rightarrow 0$. Expanding $A_{\pm 1}$ in the Taylor series in powers of E and retaining only terms linear in E , we find that the TP velocity follows

$$V_{tr} \sim \zeta^{-1} E \quad (25)$$

which relation can be thought of as the analogue of the Stokes formula for driven motion in a one-dimensional adsorbed monolayer undergoing continuous particle exchanges with the vapour phase. Equation (25) signifies that the frictional force exerted on the TP by the monolayer particles is *viscous*. The friction coefficient, i.e. the proportionality factor in equation (25), is given explicitly by

$$\zeta = \frac{2\tau}{\beta\sigma^2(1 - \rho_s)} \left[1 + \frac{\rho_s \tau^*}{\tau(f + g)} \frac{2}{1 + \sqrt{1 + 2(1 + \tau^*(1 - \rho_s)/\tau)/(f + g)}} \right]. \quad (26)$$

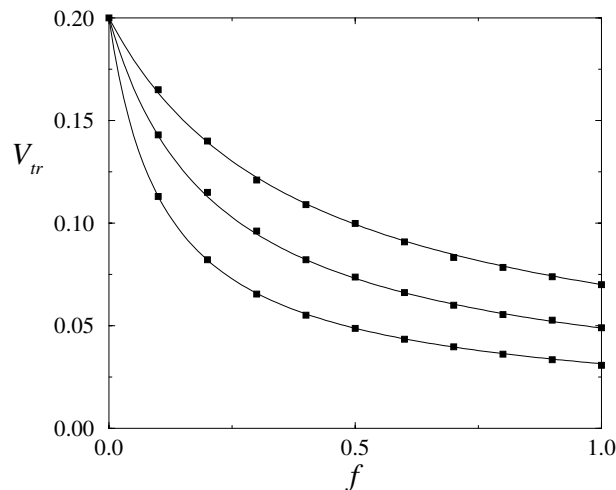


Figure 2. Terminal velocity of the tracer particle as a function of the adsorption probability f at different values of the parameter g . The probe hopping probabilities are $p_1 = 0.6$ and $p_{-1} = 0.4$. The solid lines give the analytical solution while the filled squares denote the results of Monte Carlo simulations. The upper curves correspond to $g = 0.8$, the intermediate ones to $g = 0.5$ and the lower ones to $g = 0.3$.

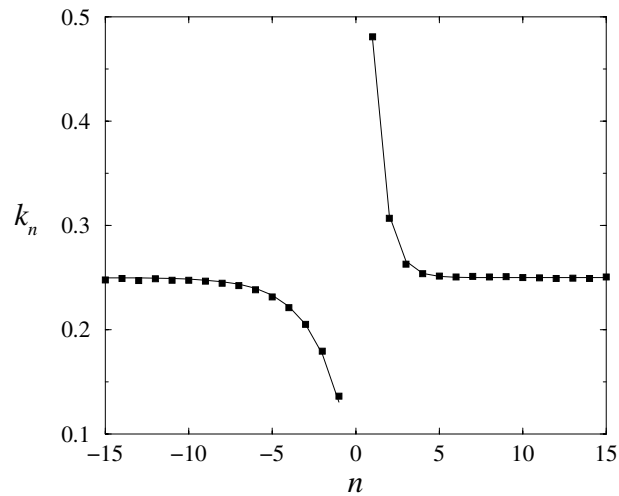


Figure 3. The density profile around a stationary moving tracer particle for $f = 0.1$, $g = 0.3$ and $p = 0.98$. The solid line is the plot of the analytical solution. The filled squares show the results of Monte Carlo simulations.

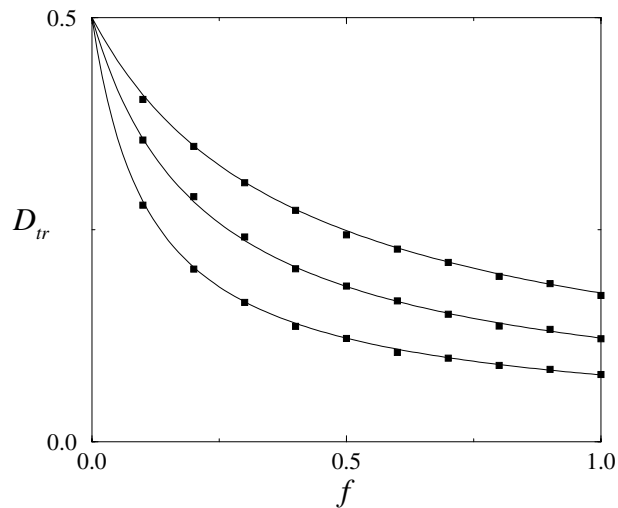


Figure 4. The self-diffusion coefficient of the tracer particle as a function of the adsorption probability f . The notation and values of g are the same as for figure 2.

Note that the friction coefficient in equation (26) can be written down as the sum of two contributions: $\zeta = \zeta_{cm} + \zeta_{coop}$. The first one, $\zeta_{cm} = 2\tau/\beta\sigma^2(1 - \rho_s)$ is a typical mean-field result and corresponds to a perfectly homogeneous monolayer (see the discussion following equation (6)). The second one,

$$\zeta_{coop} = \frac{8\tau^*\rho_s}{\beta\sigma^2(1 - \rho_s)(f + g)} \frac{1}{1 + \sqrt{1 + 2(1 + \tau^*(1 - \rho_s)/\tau)/(f + g)}} \quad (27)$$

has, however, a more complicated origin. Namely, it reflects a cooperative behaviour emerging in the monolayer, associated with the formation of inhomogeneous density profiles (see

figure 3)—the formation of a ‘traffic jam’ in front of the TP and a ‘depleted’ region past the TP (for more details, see [1]). The characteristic lengths of these two regions as well as the amplitudes K_{\pm} depend on the magnitude of the TP velocity; on the other hand, the TP velocity is itself dependent on the density profiles, by virtue of equation (5). This results in an intricate interplay between the jamming effect of the TP and smoothing of the created inhomogeneities by diffusive processes. Note also that cooperative behaviour becomes most prominent in the conserved-particle-number limit [26, 27]. Setting $f, g \rightarrow 0$, while keeping their ratio fixed (which ensures that ρ_s stays constant), one notices that ζ_{coop} becomes infinitely large. In fact, as has been shown in references [26] and [27], in such a situation no stationary density profiles around the TP exist; the sizes of both the ‘traffic jam’ and depleted regions grow in proportion to the TP mean displacement $\overline{X_{tr}(t)} \sim \sqrt{t}$ [26, 27]. Consequently, in the conserved-particle-number limit, ζ_{coop} grows indefinitely in proportion to \sqrt{t} .

In order to check our analytical predictions, we have performed numerical Monte Carlo simulations of the exact master equation of the problem, using the method of Gillespie [47]. Results of these simulations, performed at different values of the parameters f, g and p_1 , are also represented in figures 2 and 3.

Consider finally the situation with $E = 0$, in which case the terminal velocity vanishes and for which one expects conventional diffusive motion with a mean square displacement of the form

$$\overline{X_{tr}^2(t)} = 2D_{tr}t \tag{28}$$

where D_{tr} is some unknown function of the system parameters. Heuristically, we can compute D_{tr} for the system under study if we assume the validity of the Einstein relation $D_{tr} = \beta/\zeta$ between the friction coefficient and the self-diffusion coefficient D_{tr} of the TP [48], which yields

$$D_{tr} = \frac{\sigma^2(1 - \rho_s)}{2\tau} \left\{ 1 + \frac{\rho_s \tau^*}{\tau(f + g)} \frac{2}{1 + \sqrt{1 + 2(1 + \tau^*(1 - \rho_s)/\tau)/(f + g)}} \right\}^{-1}. \tag{29}$$

Monte Carlo simulations (see figure 4) of the system evidently confirm our prediction for D_{tr} given by equation (29) and, hence, confirm the validity of the Einstein relation for the system under study. This is, of course, not unexpected, but is still a non-trivial result [48].

4. Two-dimensional adsorbed monolayer

We turn now to the case of a two-dimensional substrate—adsorption onto the surface of a solid exposed to a vapour phase. Here, the situation gets somewhat more difficult from the computational point of view; we now have to solve the partial difference equation problem (17), (18) rather than the mere difference equations arising in the one-dimensional case.

The solution in two dimensions can be found in a most convenient fashion if we introduce the generating function for the particle-density profiles, defined as

$$H(w_1, w_2) \equiv \sum_{n_1=-\infty}^{+\infty} \sum_{n_2=-\infty}^{+\infty} h_{n_1, n_2} w_1^{n_1} w_2^{n_2} \tag{30}$$

where $h_{n_1, n_2} \equiv h(n_1 e_1 + n_2 e_2)$. Multiplying both sides of equations (17) and (18) by $w_1^{n_1} w_2^{n_2}$, and performing summations over n_1 and n_2 , we find that $H(w_1, w_2)$ is given explicitly by

$$H(w_1, w_2) = -K(w_1, w_2) \{A_1 w_1^{-1} + A_{-1} w_1 + A_2 (w_2 + w_2^{-1}) - \alpha\}^{-1} \tag{31}$$

where

$$\alpha \equiv \sum_{\nu} A_{\nu} + 4(f + g)$$

and

$$K(w_1, w_2) \equiv \sum_{\nu} A_{\nu} (w_{|\nu|}^{|\nu|} - 1) h(e_{\nu}) + \rho_s (A_1 - A_{-1}) (w_1 - w_1^{-1}). \quad (32)$$

Equations (31) and (32) determine the generation function for the density profiles exactly.

Before we proceed to the inversion of $H(w_1, w_2)$ with respect to the variables w_1 and w_2 , we note that we can access an interesting integral characteristic of the density profiles directly using the result in equations (31) and (32). That is, as we have already remarked, the presence of the driven TP induces an inhomogeneous density distribution in the monolayer. One can thus pose the natural question of whether the equilibrium between adsorption and desorption processes gets shifted due to such a perturbation, i.e. whether the equilibrium density in the monolayer is different from that given by equation (2). The answer is trivially ‘no’ in the case where the particle number is explicitly conserved, but in the general case with arbitrary f and g this is not at all evident: similarly to the behaviour in a one-dimensional system, one expects that in two dimensions the density profiles will also be asymmetric, as seen from the stationary moving TP, and characterized by a condensed, ‘traffic-jam’-like region in front of and a depleted region past the TP. One anticipates then that the desorption events will be favoured in front of the TP, while the adsorption events are evidently suppressed by the excess density. On the other hand, past the TP, desorption is diminished due to the particle depletion, while adsorption may proceed more readily for the same reason. It is thus not at all clear *a priori* whether these two effects can compensate for each other exactly, in view of a possible asymmetry of the density profiles, as happens in the one-dimensional model (see figure 3).

For this purpose, we study the behaviour of the integral deviation Ω of the density from the equilibrium value ρ_s ; i.e.,

$$\Omega \equiv \sum_{n_1=-\infty}^{+\infty} \sum_{n_2=-\infty}^{+\infty} h_{n_1, n_2}$$

which can be computed straightforwardly from equations (31) and (32) by setting both w_1 and w_2 equal to unity. Noticing that $K(w_1 = 1, w_2 = 1) = 0$ and that $A_1 + A_{-1} + 2A_2 - \alpha = -4(f + g)$, i.e. is strictly negative as soon as adsorption/desorption processes are present, we obtain then that Ω is strictly equal to 0. This implies, in turn, that the perturbation of the density distribution in the monolayer created by the driven TP does not shift the global balance between the adsorption and desorption events.

Inversion of the generating function with respect to w_1 and w_2 requires quite an involved mathematical analysis, which has been presented in detail in reference [4]. The general solution for the density profiles reads

$$h_{n_1, n_2} = \alpha^{-1} \left\{ \sum_{\nu} A_{\nu} h(e_{\nu}) \nabla_{-\nu} F_{n_1, n_2} - \rho_s (A_1 - A_{-1}) (\nabla_1 - \nabla_{-1}) F_{n_1, n_2} \right\} \quad (33)$$

with

$$F_{n_1, n_2} = \left(\frac{A_{-1}}{A_1} \right)^{n_1/2} \int_0^{\infty} e^{-t} I_{n_1} (2\alpha^{-1} \sqrt{A_1 A_{-1}} t) I_{n_2} (2\alpha^{-1} A_2 t) dt \quad (34)$$

where $I_n(z)$ stands for the modified Bessel function. We mention that F_{n_1, n_2} has an interesting physical interpretation in terms of the generating function of a random walk of a single particle (that is, in the absence of the particle environment) [44].

Now, equations (33) and (34) give h_{n_1, n_2} as a function of the coefficients A_ν that remain to be determined. In fact, these coefficients depend themselves on the local densities in the immediate vicinity of the tracer, i.e. on $h(e_\nu)$. This implies that we have to determine them from equations (33) and (34) in a self-consistent way [4]. Some analysis (see [4]) shows that the A_ν are determined implicitly as the solution of the following system of three non-linear matrix equations:

$$\forall \nu = \{\pm 1, 2\} \quad A_\nu = 1 + \frac{4\tau^*}{\tau} p_\nu \left\{ 1 - \rho_s - \rho_s (A_1 - A_{-1}) \frac{\det \tilde{C}_\nu}{\det \tilde{C}} \right\} \quad (35)$$

where

$$\tilde{C} = \begin{pmatrix} A_1 \nabla_{-1} F_{e_1} - \alpha & A_{-1} \nabla_1 F_{e_1} & A_2 \nabla_{-2} F_{e_1} \\ A_1 \nabla_{-1} F_{e_{-1}} & A_{-1} \nabla_1 F_{e_{-1}} - \alpha & A_2 \nabla_{-2} F_{e_{-1}} \\ A_1 \nabla_{-1} F_{e_2} & A_{-1} \nabla_1 F_{e_2} & A_2 \nabla_{-2} F_{e_2} - \alpha \end{pmatrix}. \quad (36)$$

The matrix \tilde{C}_ν stands for the matrix obtained from \tilde{C} by replacing the ν th column by the column vector \tilde{F} :

$$\tilde{F} = \begin{pmatrix} (\nabla_1 - \nabla_{-1}) F_{e_1} \\ (\nabla_1 - \nabla_{-1}) F_{e_{-1}} \\ (\nabla_1 - \nabla_{-1}) F_{e_2} \end{pmatrix} \quad (37)$$

while the local deviations $h(e_\nu)$ are expressed in terms of the A_ν as

$$h(e_\nu) = (1 - \rho_s) + \frac{\tau}{4\tau^* p_\nu} (1 - A_\nu). \quad (38)$$

Lastly, the TP terminal velocity obeys

$$V_{tr} = \frac{\sigma}{\tau} (p_1 - p_{-1}) (1 - \rho_s) \left\{ 1 + \rho_s \frac{4\tau^*}{\tau} \frac{p_1 \det \tilde{C}_1 - p_{-1} \det \tilde{C}_{-1}}{\det \tilde{C}} \right\}^{-1} \quad (39)$$

which represents the desired general force–velocity relation for the system under study, which is valid for arbitrary magnitude of the external bias and arbitrary values of other system parameters.

4.1. Asymptotical behaviour of the density profiles at large separations from the TP

The asymptotical behaviour of the density profiles at large distances from the TP follows from the analysis of the analyticity properties of the complex function

$$N(z) \equiv \sum_{n=-\infty}^{+\infty} h_{n,0} z^n.$$

It has been shown in reference [4] that in front of the TP, the deviation $h_{n,0}$ always decays exponentially with the distance:

$$h_{n,0} \sim K_+ \frac{\exp(-n/\lambda_+)}{n^{1/2}} \quad (40)$$

where the characteristic length λ_+ obeys

$$\lambda_+ = \ln^{-1} \left(\frac{1}{A_{-1}} \left\{ \frac{\alpha}{2} - A_2 + \sqrt{\left(\frac{\alpha}{2} - A_2 \right)^2 - A_1 A_{-1}} \right\} \right). \quad (41)$$

Note that λ_+ stays finite for all values of the system parameters.

In contrast, the behaviour of the density profiles at large distances past the tracer qualitatively depends on the physical situation studied. In the general case when exchanges

with the particle reservoir are allowed, the decay of the density profiles is still exponential with distance:

$$h_{-n,0} \sim K_- \frac{\exp(-n/\lambda_-)}{n^{1/2}} \quad (42)$$

where

$$\lambda_- = -\ln^{-1} \left(\frac{1}{A_{-1}} \left\{ \frac{\alpha}{2} - A_2 - \sqrt{\left(\frac{\alpha}{2} - A_2 \right)^2 - A_1 A_{-1}} \right\} \right). \quad (43)$$

Note that in the general case the characteristic lengths, again similarly to the one-dimensional case, satisfy the inequality $\lambda_- > \lambda_+$, which means that the correlations between the TP and the particles of the monolayer are always stronger past than in front of the TP.

Such correlations can even become extremely strong in the special case where the particle exchanges with the vapour phase are forbidden, i.e. in the conserved-particle-number limit, which can be realized for monolayers sandwiched in a narrow gap between two solid surfaces. In this case, we have that λ_- becomes infinitely large and, in the limit $n \rightarrow +\infty$, the deviation of the particle density from the equilibrium value ρ_s follows

$$h_{-n,0} = -\frac{K'_-}{n^{3/2}} \left(1 + \frac{3}{8n} + \mathcal{O}\left(\frac{1}{n^2}\right) \right). \quad (44)$$

Remarkably enough, in this case the correlations between the TP position and the particle distribution vanish *algebraically* slowly with the distance! This implies, in turn, that in the conserved-particle-number case, the mixing of the monolayer is not efficient enough to prevent the appearance of the quasi-long-range order and the medium ‘remembers’ the passage of the TP on a long scale of time and space, which signifies very strong memory effects.

4.2. Limit of small applied force

We turn now to the limit $\beta E \ll 1$, in which case the problem simplifies considerably, which allows us to obtain explicit results for the local densities in the immediate vicinity of the TP and, consequently, for the TP terminal velocity and its diffusivity.

In this limit, we arrive again at a Stokes-type formula of the form $V_{tr} \sim E/\zeta$, where now

$$\zeta = \frac{4\tau}{\beta\sigma^2(1-\rho_s)} \left\{ 1 + \frac{\tau^*}{\tau} \frac{\rho_s}{(f+g+1+\tau^*(1-\rho_s)/\tau)(\mathcal{L}(x)-x)} \right\} \quad (45)$$

with

$$x = \frac{1}{2} \frac{1 + \tau^*(1-\rho_s)/\tau}{f + g + 1 + \tau^*(1-\rho_s)/\tau} \quad (46)$$

and

$$\mathcal{L}(x) \equiv \left\{ \int_0^\infty e^{-t} (I_0(xt) - I_2(xt)) I_0(xt) dt \right\}^{-1}. \quad (47)$$

Note that we are again able to single out two physically meaningful contributions to the friction coefficient ζ . That is, the first term on the rhs of equation (45) is just the mean-field-type result corresponding to a perfectly stirred monolayer, in which correlations between the TP and the monolayer particles are discarded. The second term, similarly to the one-dimensional case, mirrors the cooperative behaviour emerging in the monolayer and is associated with the backflow effects. In contrast to the one-dimensional case, however, the contribution to the overall friction coefficient stemming from the cooperative effects remains finite in the conserved-particle-number limit.

We also wish to remark that a qualitatively similar physical effect has been predicted recently for a different model system involving a charged particle moving at a constant speed a small distance above the surface of an incompressible, infinitely deep liquid. It has been shown in references [45,46] that the interactions between the moving particle and the fluid molecules induce an effective frictional force exerted on the particle, producing a local distortion of the liquid interface—a bump, which travels together with the particle and effectively increases its mass. The mass of the bump, which is analogous to the jammed region appearing in our model, itself depends on the particle's velocity, resulting in a non-linear coupling between the medium-induced frictional force exerted on the particle and its velocity [45,46].

Lastly, assuming *a priori* that the Einstein relation holds for the system under study, we estimate the TP diffusion coefficient $D_{tr} = \beta^{-1}\zeta^{-1}$ as

$$D_{tr} = \frac{\sigma^2}{4\tau}(1 - \rho_s) \left\{ 1 - \frac{2\rho_s\tau^*}{\tau} \frac{1}{4(f + g + 1 + \tau^*(1 - \rho_s)/\tau)\mathcal{L}(x) - 1 + (3\rho_s - 1)\tau^*/\tau} \right\}. \quad (48)$$

It now seems interesting to compare our general result in equation (48) against the classical result of Nakazato and Kitahara [22], which describes the TP diffusion coefficient in a two-dimensional lattice gas with conserved particle number. Setting f and g equal to zero, while assuming that their ratio has a fixed value, $f/g = \rho_s/(1 - \rho_s)$, we have then that

$$\hat{D}_{tr} = \frac{\sigma^2}{4\tau}(1 - \rho_s) \left\{ 1 - \frac{2\rho_s\tau^*}{\tau} \frac{1}{4(1 + \tau^*(1 - \rho_s)/\tau)\mathcal{L}(1/2) - 1 + (3\rho_s - 1)\tau^*/\tau} \right\}. \quad (49)$$

Using next the equality [49]:

$$\mathcal{L}(1/2) = \frac{\pi}{4(\pi - 2)} \quad (50)$$

we find that the right-hand side of equation (49) attains the form

$$\hat{D}_{tr} = \frac{\sigma^2}{4\tau}(1 - \rho_s) \left\{ 1 - \frac{2\rho_s\tau^*}{\tau} \frac{1 - 2/\pi}{1 + (1 - \rho_s)\tau^*/\tau - (1 - 2/\pi)(1 + (1 - 3\rho_s)\tau^*/\tau)} \right\} \quad (51)$$

which expression coincides exactly with the earlier result obtained in references [22] and [23] within the framework of a different—compared to ours—analytical technique. The result in equation (51) is known to be exact in the limits $\rho_s \ll 1$ and $\rho_s \sim 1$, and serves as a very good approximation for the self-diffusion coefficient for hard-core lattice gases of arbitrary density [21], which supports in a way the validity of the approximation invoked in equation (9).

5. Conclusions

To conclude, we have studied analytically the intrinsic frictional properties of adsorbed monolayers, composed of mobile hard-core particles undergoing continuous exchanges with the vapour. Our analytical approach has been based on the master equation, describing the time evolution of the system, which has allowed us to evaluate a system of coupled dynamical equations for the TP velocity and a hierarchy of correlation functions. To solve these coupled equations, we have invoked an approximate closure scheme based on the decomposition of the third-order correlation functions into a product of pairwise correlations, which was first introduced in reference [26] for a related model of a driven tracer particle dynamics in a one-dimensional lattice gas with conserved particle number. Within the framework of this approximation, we have derived a system of coupled, discrete-space equations describing evolution of the density profiles in the adsorbed monolayer, as seen from the moving tracer, and its velocity V_{tr} . We have shown that the density profile around the tracer is strongly

inhomogeneous: the local density of the adsorbed particles in front of the tracer is higher than the average and approaches the average value as an exponential function of the distance from the tracer. On the other hand, past the tracer the local density is always lower than the average and, depending on whether the number of particles is explicitly conserved or not, the local density past the tracer may tend to the average value either as an exponential or even as an *algebraic* function of the distance. The latter reveals especially strong memory effects and strong correlations between the particle distribution in the environment and the carrier position. Next, we derived a general force–velocity relation, which defines the terminal velocity of the tracer particle for arbitrary applied fields and arbitrary values of other system parameters. We demonstrated next that in the limit of a vanishingly small external bias this relation attains the simple, but physically meaningful form of the Stokes formula, which signifies that in this limit the frictional force exerted on the tracer by the adsorbed monolayer particles is viscous. The corresponding friction coefficient has also been explicitly determined. In addition, we estimated the self-diffusion coefficient of the tracer in the absence of the field and showed that it reduces to the well-known result of references [22] and [23] in the limit where the particle number is conserved.

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