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 vapor 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, define the frictional forces as well as the particles 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 confirms 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 vapor phase \[1-4\]. Such layers are involved in various technological and material processing operations, including, for instance, coating, gluing or lubrication. Knowledge of their intrinsic frictional properties is important for conceptual understanding of different transport processes taking place within molecular films, film’s stability, as well as spreading of ultrathin liquid films on solid surfaces \[3, 8\], spontaneous or forced dewetting of monolayers \[7-10\] or 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 the adsorbed films \[12-16\]. Here, significant analytical results have been obtained predicting different phase transitions and ordering phenomena, which well agree with the available experimental data. As well, some approximate results have been obtained for both dynamics of an isolated adatom on a corrugated surface and collective diffusion, describing spreading of the macroscopic density fluctuations in interacting adsorbates being in contact with the vapor \[17-20\].

Another important aspect of dynamical behavior concerns tracer diffusion in adsorbates, which is observed experimentally in STM or field ion measurements and provides a useful information about 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 behavior, but is also crucial for understanding of various dynamical processes taking place on solid surfaces. However, most of available theoretical studies of tracer diffusion in adsorbed layers (see, e.g. Refs.\[21-29\]) do exclude the possibility of particles exchanges with the vapor.

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 vapor phase - a reservoir of particles. More specifically, the system we consider consists of (a) a solid substrate, which is modeled in a usual fashion as a regular lattice of adsorption sites; (b) a monolayer of adsorbed, mobile hard-core particles in contact with a vapor and (c) a single hard-core tracer particle (TP). We suppose that the monolayer particles move randomly along the lattice by performing symmetric hopping motion between the neighboring lattice sites, which process is constrained by mutual hard-core interactions, and may desorb from and adsorb onto the lattice from the vapor with some prescribed rates dependent on the
vapor pressure, temperature and the interactions with the solid substrate. In contrast, the tracer particle is constrained to move along the lattice only, (i.e. it can not desorb to the vapor), and is subject to a constant external force of an 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 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 $t \to \infty$, 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 particles density distribution in the monolayer. As a matter of fact, we proceed to show that there are stationary density profiles around the TP as $t \to \infty$, which mirror a remarkable cooperative behavior.

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. Ref.\[21\] 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 of 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 influence itself 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 being in contact with a solid body. It is well known (see, e.g., Ref. [36]) that liquids in close vicinity of a solid interfaces - at distances within a few molecular diameters, do possess completely different physical properties compared to these of the bulk phase. In this “stagnant” region, in which an intrinsically disordered liquid phase is spanned by and contends with the ordering potential of the solid, liquid’s viscosity is drastically enhanced and transport processes, (regarding, say, biased diffusion of charged carriers in solutions), are essentially 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 in case of a two-dimensional solid substrate and introduce basic notations. We write down then 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 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 identic, electrically neutral particles - a vapor phase (Fig.1), maintained at a constant pressure. For simplicity of exposition, we assume here that adsorption sites form a regular square lattice of spacing \(\sigma\). We suppose next that the reservoir particles may adsorb onto any vacant adsorption site at a fixed rate \(f/\tau^*\), which rate depends on the vapor pressure and the energy gain due to the adsorption event. Further on, the adsorbed particles may move randomly along the lattice by hopping at a rate \(1/4\tau^*\) to any of 4 neighboring adsorption sites, which process is constrained by hard-core exclusion preventing multiple occupancy of any of the sites. Lastly, the adsorbed
particles may desorb from the lattice back to the reservoir at rate $g/\tau^*$, which is dependent on the barrier against desorption. Both $f$ and $g$ are site and environment independent.

Figure 1: Adsorbed monolayer in contact with a vapor. Grey spheres denote the monolayer (vapor) particles; the smaller black sphere stands for the driven tracer particle.

Note that such a model represents, of course, a certain idealization. In "real world" systems, the adsorbed particles experience two types of interactions: 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 harsh repulsion at short scales, and are attractive at longer distances. The SP repulsion keeps the adsorbed particles some distance apart of the solid, while the SP attraction favors adsorption and hinders particles 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 particles desorption (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 neighborhood; after the jump is performed, the particle dissipates all its energy to the host solid. Thus, on a macroscopic time scale the particles do not possess any velocity. The time $\tau^*$ separating two successive jump events, is just the typical time a given particle spends in a given well vibrating around its minimum; $\tau^*$ 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 a type of random motion is essentially different from the standard hydrodynamic picture of particles 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 neighbors, along a lattice-like structure of such cells (see, e.g. Refs. [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 realistic systems, of course, both the particle-particle scattering and 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 [12, 13]. 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. As a matter of 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 particles dynamics is inappropriate under the defined above physical conditions. Contrary to that, any adsorbed particle moves due to random hopping events, activated by chaotic vibrations of the solid atoms, along the local minima of an array of potential wells, created due to the interactions with the solid [13, 16]. As we have already remarked, in the physical conditions under which such a dynamics takes place, the PP interactions are much weaker than the SP interactions and hence do not perturb significantly the regular array of potential wells due to the SP interactions. In our model, we discard completely the attractive part of the PP interac-
tion 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 $\eta(R)$, which may assume two values:

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

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

$$\rho_s = \frac{f}{f + g} \quad (1)$$

This relation is well known and represents the customary Langmuir adsorption isotherm
[12]. We finally remark that in the analysis of the stationary-state behavior, we can always
turn to the conserved particles 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 particles density $\rho_s$,
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; position of this particle at time $t$ is denoted as $R_{tr}$. 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 aspects:
first, it can not desorb from the lattice and second, it is subject to some external driving
force, which favors its jumps into a preferential direction. Physically, such a situation may
be realized, for instance, if this only particle is charged and the system is subject to a
uniform electric field $E$. We suppose here, for simplicity of exposition, that the external
force $E$ is oriented according to the unit vector $e_1$. 
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 $\tau$, and then attempts to hop onto one of 4 neighboring sites, $\mathbf{R}_{tr} + \mathbf{e}_\nu$, where $\mathbf{e}_\nu$ are 4 unit vectors of the hypercubic lattice. In what follows we adopt the notation $\nu = \{\pm 1, \pm 2\}$, where $\pm \mathbf{e}_1$ will denote the direction of the external force $\mathbf{E}$. Next, the jump direction is chosen according to the probability $p_\nu$, which obeys:

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

where $\beta$ 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 $\mu$ denotes summation over all possible orientations of the vector $\mathbf{e}_\mu$; 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 fulfilled 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 behavior 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 time 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 $\eta$. Then, denoting as $\eta^{r,\nu}$ a configuration obtained from $\eta$ by the Kawasaki-type exchange of the occupation variables of two neighboring sites $\mathbf{r}$ and $\mathbf{r} + \mathbf{e}_\nu$, and as $\hat{\eta}^r$ - a configuration obtained from the original $\eta$ by the replacement $\eta(\mathbf{r}) \rightarrow 1 - \eta(\mathbf{r})$, 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
The following master equation:
\[ \frac{\partial}{\partial t} P(\mathbf{R}_{tr}, \eta; t) = \frac{1}{2d\tau^*} \sum_{\mu=1}^{d} \sum_{\mathbf{r} \neq \mathbf{R}_{tr} - \mathbf{e}_{\mu}, \mathbf{R}_{tr}} \{ P(\mathbf{R}_{tr}, \eta^r_{\mu}; t) - P(\mathbf{R}_{tr}, \eta; t) \} \]
\[ + \frac{1}{\tau} \sum_{\mu} p_{\mu} \left\{ (1 - \eta(\mathbf{R}_{tr})) P(\mathbf{R}_{tr} - \mathbf{e}_{\mu}, \eta; t) - (1 - \eta(\mathbf{R}_{tr} + \mathbf{e}_{\mu})) P(\mathbf{R}_{tr}, \eta; t) \right\} \]
\[ + \frac{g}{\tau^*} \sum_{\mathbf{r} \neq \mathbf{R}_{tr}} \left\{ (1 - \eta(\mathbf{r})) P(\mathbf{R}_{tr}, \eta^{\mathbf{r}}; t) - \eta(\mathbf{r}) P(\mathbf{R}_{tr}, \eta; t) \right\} \]
\[ + \frac{f}{\tau^*} \sum_{\mathbf{r} \neq \mathbf{R}_{tr}} \left\{ \eta(\mathbf{r}) P(\mathbf{R}_{tr}, \hat{\eta}^{\mathbf{r}}; t) - (1 - \eta(\mathbf{r})) P(\mathbf{R}_{tr}, \eta; t) \right\}. \] (3)

The mean velocity \( V_{tr}(t) \) of the TP can be obtained by multiplying both sides of Eq.(3) by \((\mathbf{R}_{tr} \cdot \mathbf{e}_1)\) and summing over all possible configurations \((\mathbf{R}_{tr}, \eta)\). This results in the following exact equation determining the TP velocity:
\[ V_{tr}(t) = \frac{d}{dt} \sum_{\mathbf{R}_{tr}, \eta} (\mathbf{R}_{tr} \cdot \mathbf{e}_1) P(\mathbf{R}_{tr}, \eta; t) = \frac{\sigma}{\tau} \left\{ p_1 \left( 1 - k(\mathbf{e}_1; t) \right) - p_{-1} \left( 1 - k(\mathbf{e}_{-1}; t) \right) \right\}, \] (4)
where
\[ k(\lambda; t) \equiv \sum_{\mathbf{R}_{tr}, \eta} \eta(\mathbf{R}_{tr} + \lambda) P(\mathbf{R}_{tr}, \eta; t) \] (5)
is the probability of having at time \( t \) an adsorbed particle at position \( \lambda \), defined in the frame of reference moving with the TP. In other words, \( k(\lambda; t) \) can be thought of as being the density profile in the adsorbed monolayer as seen from the moving TP.

Equation (4) signifies that the velocity of the TP is dependent on the monolayer particles density in the immediate vicinity of the tracer. If the monolayer is perfectly stirred, or, in other words, if \( k(\lambda; t) = \rho_s \) everywhere, (which implies immediate decoupling of \( \mathbf{R}_{tr} \) and \( \eta \)), one would obtain from Eq.(4) a trivial mean-field result
\[ V^{(0)}_{tr} = (p_1 - p_{-1})(1 - \rho_s) \frac{\sigma}{\tau}, \] (6)
which states that the only effect of the medium on the TP dynamics is that its jump time \( \tau \) 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, \( k(\lambda; t) \) is different from the equilibrium value \( \rho_s \) everywhere, except for \( |\lambda| \to \infty \). This
means that the TP strongly perturbs the particles 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 particles density at the neighboring to the TP sites \( \mathbf{R}_{tr} + \mathbf{e}_{\pm 1} \), which requires, in turn, computation of the density profile \( k(\mathbf{\lambda}; t) \) for arbitrary \( \mathbf{\lambda} \). The latter can be found from the master equation (3) by multiplying both sides by \( \eta(\mathbf{R}_{tr}) \) and performing the summation over all configurations \( (\mathbf{R}_{tr}, \eta) \). In doing so, we find that these equations are not closed with respect to \( k(\mathbf{\lambda}; t) \), but are coupled to the third-order correlations,

\[
T(\mathbf{\lambda}, \mathbf{e}_\nu; t) = \sum_{\mathbf{R}_{tr}, \eta} \eta(\mathbf{R}_{tr} + \mathbf{\lambda}) \eta(\mathbf{R}_{tr} + \mathbf{e}_\mu) P(\mathbf{R}_{tr}, \eta; t) \tag{7}
\]

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 \( k(\mathbf{\lambda}; t) \), which has been first proposed in Refs.\[26\] and \[27\], and represent \( T(\mathbf{\lambda}, \mathbf{e}_\nu; t) \) as

\[
\sum_{\mathbf{R}_{tr}, \eta} \eta(\mathbf{R}_{tr} + \mathbf{\lambda}) \eta(\mathbf{R}_{tr} + \mathbf{e}_\mu) P(\mathbf{R}_{tr}, \eta; t) \approx \left( \sum_{\mathbf{R}_{tr}, \eta} \eta(\mathbf{R}_{tr} + \mathbf{\lambda}) P(\mathbf{R}_{tr}, \eta; t) \right) \left( \sum_{\mathbf{R}_{tr}, \eta} \eta(\mathbf{R}_{tr} + \mathbf{e}_\mu) P(\mathbf{R}_{tr}, \eta; t) \right) = k(\mathbf{\lambda}; t) k(\mathbf{e}_\mu; t), \tag{8}
\]

Some arguments justifying such an approximation \textit{a posteriori} are presented in Sections 3 and 4 (see also Ref.\[3\]).

Using the approximation in Eq.(8), we obtain

\[
2d\tau^* \partial_t k(\mathbf{\lambda}; t) = \tilde{L} k(\mathbf{\lambda}; t) + 2df, \tag{9}
\]

which holds for all \( \mathbf{\lambda} \), except for \( \mathbf{\lambda} = \{ \mathbf{0}, \pm \mathbf{e}_1, \mathbf{e}_2, \ldots, \mathbf{e}_d \} \). One the other hand, for these special sites \( \mathbf{\lambda} = \mathbf{e}_\nu \) with \( \nu = \{ \pm 1, 2, \ldots, d \} \) we find

\[
2d\tau^* \partial_t k(\mathbf{e}_\nu; t) = (\tilde{L} + A_\nu) k(\mathbf{e}_\nu; t) + 4f, \tag{10}
\]

where \( \tilde{L} \) is the operator

\[
\tilde{L} \equiv \sum_\mu A_\mu \nabla_\mu - 4(f + g), \tag{11}
\]
and the coefficients $A_{\mu}$ are defined by
\[ A_{\mu}(t) \equiv 1 + \frac{2d\tau^*}{\tau}p_{\mu}(1 - k(\mathbf{e}_\mu; t)). \]  
\hspace{1cm} (12)

Note that Eq.(10) represents, from the mathematical point of view, the boundary conditions for the general evolution equation (9), imposed on the sites in the immediate vicinity of the TP. Equations (9) and (10) together with Eq.(4) thus constitute a closed system of equations which suffice computation of all properties of interest.

### 2.3 Stationary solution of the evolution equations

We turn to the limit $t \to \infty$ and suppose that both the density profiles and stationary velocity of the TP have non-trivial stationary values
\[ k(\lambda) \equiv \lim_{t \to \infty} k(\lambda; t), \quad V_{tr} \equiv \lim_{t \to \infty} V_{tr}(t), \quad \text{and} \quad A_{\mu} \equiv \lim_{t \to \infty} A_{\mu}(t) \]  
\hspace{1cm} (13)

Define next the local deviations of $k(\lambda)$ from the unperturbed density as
\[ h(\lambda) \equiv k(\lambda) - \rho_s \]  
\hspace{1cm} (14)

Choosing that $h(0) = 0$, we obtain then the following fundamental system of equations:
\[ \tilde{L}h(\lambda) = 0 \quad \text{for all} \quad \lambda \neq \{0, e_{\pm 1}, \ldots, e_{\pm d}\}, \]  
\hspace{1cm} (15)

\[ (\tilde{L} + A_{\nu})h(\mathbf{e}_\nu) + \rho_s(A_{\nu} - A_{-\nu}) = 0 \quad \text{for} \quad \lambda = \{0, e_{\pm 1}, \ldots, e_{\pm d}\}, \]  
\hspace{1cm} (16)

which determine the deviation from the unperturbed density $\rho_s$ in the stationary state. Note also that in virtue of an evident symmetry, $h(\mathbf{e}_\nu) = h(\mathbf{e}_{-\nu})$ and $A_{\nu} = A_{-\nu}$ for $\nu \in \{2, \ldots, d\}$.

The general approach to solution of coupled non-linear Eqs.(4), (15) and (16) has been discussed in detail in Ref.[4]. Here we merely note that despite the fact that using the decoupling scheme in Eq.(8) we effectively close the system of equations on the level of the pair correlations, solution of Eqs.(15) and (16) (or, equivalently, of Eqs.(9) and (10)) 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 does depend itself on the values of the monolayer particles densities in the immediate vicinity of the TP. Solution of this system of non-linear equation for one- and two-dimensional substrates is displayed in two next sections.
3 One-dimensional adsorbed monolayer

For one-dimensional lattices, which which situation is appropriate to adsorption on polymer chains \[37, 38\], general solution of Eqs.(15) and (16) has the following form:

\[ k_n \equiv k(\lambda) = \rho_s + K_\pm \exp \left(-\sigma |n|/\lambda_\pm \right), \quad \lambda = \sigma n, \quad n \in \mathbb{Z}, \quad (17) \]

where the characteristic lengths \( \lambda_\pm \) obey

\[ \lambda_\pm = \mp \sigma \ln^{-1} \left[ \frac{A_1 + A_{-1} + 2(f + g) \mp \sqrt{(A_1 + A_{-1} + 2(f + g))^2 - 4A_1A_{-1}}}{2A_1} \right], \quad (18) \]

while the amplitudes \( K_\pm \) are given respectively by

\[ K_+ = \rho_s \frac{A_1 - A_{-1}}{A_{-1} - A_1 \exp(-\sigma/\lambda_+)} \quad (19) \]

and

\[ K_- = \rho_s \frac{A_1 - A_{-1}}{A_{-1} \exp(-\sigma/\lambda_-) - A_1} \quad (20) \]

Note that \( \lambda_- > \lambda_+ \), and consequently, the local density past the TP approaches its non-perturbed value \( \rho_s \) slower than 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-monotoneous function of \( \lambda \) and is characterized by a jammed region in front of the TP, in which the local density is higher than \( \rho_s \), and a depleted region past the TP in which the density is lower than \( \rho_s \).

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 \( A_\pm \) through \( V_{tr} = \sigma (A_1 - A_{-1})/2\tau^* \). Substituting Eq.(17) into Eq.(12), we find

\[ A_1 = 1 + \frac{p_1\tau^*}{\tau} \left[ 1 - \rho_s - \rho_s \frac{A_1 - A_{-1}}{A_{-1} \exp(\sigma/\lambda_+) - A_1} \right] \quad (21) \]

and

\[ A_{-1} = 1 + \frac{p_{-1}\tau^*}{\tau} \left[ 1 - \rho_s - \rho_s \frac{A_1 - A_{-1}}{A_{-1} - A_1 \exp(\sigma/\lambda_-)} \right] \quad (22) \]
Figure 2: Terminal velocity of the probe molecule 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. Upper curves correspond to $g = 0.8$, the intermediate - to $g = 0.5$ and the lower - to $g = 0.3$, respectively.

Resolution of this system leads then to the stationary velocity of the TP (see Fig.2) as well as the density profiles (see Fig.3). For arbitrary values of $p$, $f$ and $g$ the parameters $A_{\pm 1}$, defined by Eqs.(21) and (22), and consequently, the terminal velocity $V_{tr}$ can be determined only numerically (see Figs.2 to 4). However, $V_{tr}$ can be found analytically in the explicit form in the limit of a vanishingly small force $E$, $E \to 0$. Expanding $A_{\pm 1}$ in the Taylor series in powers of $E$ and retaining only linear with $E$ terms, we find that the TP velocity follows

$$V_{tr} \sim \zeta^{-1}E,$$

which relation can be thought off as the analog of the Stokes formula for driven motion in a one-dimensional adsorbed monolayer undergoing continuous particles exchanges with the vapor phase. Equation (23) signifies that the frictional force exerted on the TP by the monolayer particles is *viscous*. The friction coefficient, i.e. the proportionality factor in
Eq. (23) is given explicitly by
\[ \zeta = \frac{2\tau}{\beta \sigma^2 (1 - \rho_s)} \left[ 1 + \frac{\rho_s \tau^*}{\tau (f + g)} \frac{2}{1 + \sqrt{1 + 2(1 + \tau^*(1 - \rho_s)/\tau)/(f + g)}} \right] \] (24)

Note that the friction coefficient in Eq. (24) 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 discussion following Eq. (5)). The second one,
\[ \zeta_{coop} = \frac{8\tau^* \rho_s}{\beta \sigma^2 (1 - \rho_s) (f + g)} \frac{1}{1 + \sqrt{1 + 2(1 + \tau^*(1 - \rho_s)/\tau)/(f + g)}} \] (25)

has, however, a more complicated origin. Namely, it reflects a cooperative behavior emerging in the monolayer, associated with the formation of inhomogeneous density profiles (see Fig. 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, in virtue of Eq. (4). 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 behavior becomes most prominent in the conserved particle number limit [26, 27]. Setting \( f, g \to 0 \), while keeping their ratio fixed (which insures that \( \rho_s \) stays constant), one notices that \( \zeta_{coop} \) gets infinitely large. As a matter of fact, as it has been shown in Refs. [26] and [27], in such a situation no stationary density profiles around the TP exist; the size of both the ”traffic jam” and depleted regions grow in proportion to the TP mean displacement \( X_{tr}(t) \sim \sqrt{t} \) [26, 27]. Consequently, in the conserved particle number limit \( \zeta_{coop} \) 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 Figs. 2 and 3.

Consider finally the situation with \( E = 0 \), in which case the terminal velocity vanishes and one for which one expects conventional diffusive motion with the mean square displacement of the form
\[ \overline{X_{tr}^2(t)} = 2D_{tr}t, \] (26)
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

$$D_{tr} = \frac{\sigma^2(1 - \rho_s)}{2\tau} \left\{ 1 + \frac{\rho_s\tau^*}{\tau(f + g)} \frac{2}{1 + \sqrt{1 + 2(1 + \tau^*(1 - \rho_s)/\tau)/(f + g)}} \right\}^{-1}. \quad (27)$$

Monte Carlo simulations (see Fig.4) of the system evidently confirm our prediction for $D_{tr}$ given by Eq.(27), and hence, confirm the validity of the Einstein relation for the system under study. This is, of course, not an unexpected, but 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 vapor phase. Here, the situation gets somewhat more difficult from the computational point of view; we have now to solve the partial difference equations problem ([15], [16]) rather than the mere difference equations arising in the one-dimensional case.
Figure 4: Self-diffusion coefficient of the probe molecule as a function of the adsorption probability $f$. Notations and values of $g$ are the same as in Figs.3.

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

$$H(w_1, w_2) \equiv \sum_{n_1=-\infty}^{+\infty} \sum_{n_2=-\infty}^{+\infty} h_{n_1,n_2} w_1^{n_1} w_2^{n_2}, \quad (28)$$

where $h_{n_1,n_2} \equiv h(n_1 e_1 + n_2 e_2)$. Multiplying both sides of Eqs. (15) and (16) 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

$$H(w_1, w_2) = -K(w_1, w_2) \left\{ A_1 w_1^{-1} + A_{-1} w_1 + A_2 (w_2 + w_2^{-1}) - \alpha \right\}^{-1}, \quad (29)$$

where $\alpha \equiv \sum_\nu A_\nu + 4(f + g)$ and

$$K(w_1, w_2) \equiv \sum_\nu A_\nu (w_\nu^{\nu/|\nu|} - 1) h(e_\nu) + \rho_s (A_1 - A_{-1}) (w_1 - w_1^{-1}). \quad (30)$$

Equations (29) and (30) 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 interesting integral characteristic of the density profiles directly using the result in Eqs. (29) and (30). Namely, as we have already remarked, the presence of the driven TP induces an inhomogeneous density distribution in the monolayer. One
can thus pose a natural question whether equilibrium between adsorption and desorption processes gets shifted due to such a perturbancy, i.e. whether the equilibrium density in the monolayer is different from that given by Eq.(1). The answer is trivially "no" in the case when the particles number is explicitly conserved, but in the general case with arbitrary \( f \) and \( g \) this is not at all evident: similarly to the behavior in one-dimensional system one expects that also in two-dimensions the density profiles are asymmetric as seen from the stationary moving TP and are 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 are favored 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 particles depletion while adsorption may proceed more readily due to the same reason. It is thus not at all clear \textit{a priori} whether these two effects can compensate each other exactly, in view of a possible asymmetry of the density profiles, as it happens in the one-dimensional model (see Fig.3).

For this purpose, we study the behavior of the integral deviation \( \Omega \) of the density from the equilibrium value \( \rho_s \), 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 Eqs.(29) and (30) 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 \( \Omega \) is strictly equal to 0. This implies, in turn, that the perturbancy 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 Ref.[4]. General solution for the density profiles reads:

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

with

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

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 absence of the particles environment) [44].

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Now, the Eqs. (31) and (32) display $h_{n_1, n_2}$ as a function of the coefficients $A_\nu$ that remain to be determined. As a matter of 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 Eqs. (31) and (32) in a self-consistent way [4]. Some analysis (see [4]) shows that $A_\nu$ are determined implicitly as the solution of the following system of three non-linear matrix equations
\[ \forall \nu = \{\pm 1, 2\}, \quad A_\nu = 1 + \frac{4\tau^* p_\nu}{\tau} \left\{ 1 - \rho_s - \rho_s(A_1 - A_{-1}) \frac{\det \tilde{C}_\nu}{\det \tilde{C}} \right\}, \] (33)
where
\[ \tilde{C} = \begin{pmatrix} A_1 \nabla_1 F_{e_1} - \alpha & A_{-1} \nabla_1 F_{e_1} & A_2 \nabla_{-2} F_{e_1} \\ A_1 \nabla_{-1} F_{e_{-1}} & A_{-1} \nabla_{-1} F_{e_{-1}} - \alpha & A_2 \nabla_{-2} F_{e_{-1}} \\ A_1 \nabla_{-1} F_{e_2} & A_{-1} \nabla_{-1} F_{e_2} & A_2 \nabla_{-2} F_{e_2} - \alpha \end{pmatrix}. \] (34)
the matrix $\tilde{C}_\nu$ stands for the matrix obtained from $\tilde{C}$ by replacing the $\nu$-th column by the column-vector $\tilde{F}$,
\[ \tilde{F} = \begin{pmatrix} (\nabla_1 - \nabla_{-1}) F_{e_1} \\ (\nabla_1 - \nabla_{-1}) F_{e_{-1}} \\ (\nabla_1 - \nabla_{-1}) F_{e_2} \end{pmatrix}, \] (35)
while the local deviations $h(e_\nu)$ are expressed in terms of $A_\nu$ as
\[ h(e_\nu) = (1 - \rho_s) + \frac{4\tau^* p_\nu}{\tau}(1 - A_\nu). \] (36)
Lastly, the TP terminal velocity obeys
\[ V_{tr} = \frac{\sigma}{\tau}(p_1 - p_{-1})(1 - \rho_s) \left\{ 1 + \rho_s \frac{4\tau^* p_1 \det \tilde{C}_1 - p_{-1} \det \tilde{C}_{-1}}{\tau \det \tilde{C}} \right\}^{-1}, \] (37)
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’s parameters.

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

Asymptotical behavior of the density profiles at large distances from the TP follows from the analysis of the analyticity properties of the complex function $N(z) \equiv \sum_{n=-\infty}^{+\infty} h_{n,0} z^n$. 

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

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

where the characteristic length $\lambda_+$ obeys:

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

Note that $\lambda_+$ stays finite for any values of the system parameters.

On contrary, the behavior 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 particles reservoir are taken into allowed, the decay of the density profiles is still exponential with the distance:

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

where

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

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 when the particles exchanges with the vapor phase are forbidden, i.e. in the conserved particles number limit, which can be realized for the monolayers sandwiched in a narrow gap between two solid surfaces. In this case, we have that $\lambda_-$ becomes infinitely large and, in the limit $n \to +\infty$, the deviation of the particle density from the equilibrium value $\rho_s$ follows

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

Remarkably enough, in this case the correlations between the TP position and the particles distribution vanish algebraically slow with the distance! This implies, in turn, that in the conserved particles 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 time and space scale, 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 and allows 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

$$\zeta = \frac{4\tau}{\beta \sigma^2(1 - \rho_s)} \left\{ 1 + \frac{\tau^*}{\tau} \frac{\rho_s}{f + g + 1 + \tau^*(1 - \rho_s)/\tau} \left( L(x) - x \right) \right\}, \quad (43)$$

with

$$x = \frac{1}{2} \frac{1 + \tau^*(1 - \rho_s)/\tau}{f + g + 1 + \tau^*(1 - \rho_s)/\tau}, \quad (44)$$

and

$$L(x) \equiv \left\{ \int_0^\infty e^{-t} \left( (I_0(xt) - I_2(xt))I_0(xt) \right) dt \right\}^{-1}. \quad (45)$$

Note that we again are able to single out two physical meaningful contributions to the friction coefficient $\zeta$. Namely, the first term on the rhs of Eq. (43) 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 behavior 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 out of the cooperative effects remains finite in the conserved particles 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 Refs. [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 increases effectively its mass. The mass of the bump, which is analogous to the jammed region appearing in our model, depends itself 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

$$D_{tr} = \frac{\sigma^2}{4\tau} (1 - \rho_s) \left\{ 1 - \frac{2\rho_s \tau^*}{\tau} \frac{1}{4(f + g + 1 + \tau^*(1 - \rho_s)/\tau) \mathcal{L}(x) - 1 + (3\rho_s - 1)\tau^*/\tau} \right\}. \quad (46)$$

It seems now interesting to compare our general result in Eq.(46) against the classical result of Nakazato and Kitahara [22], which describes TP diffusion coefficient in a two-dimensional lattice gas with conserved particles 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

$$\hat{D}_{tr} = \frac{\sigma^2}{4\tau} (1 - \rho_s) \left\{ 1 - \frac{2\rho_s \tau^*}{\tau} \frac{1}{4 + \tau^*(1 - \rho_s)/\tau) \mathcal{L}(1/2) - 1 + (3\rho_s - 1)\tau^*/\tau} \right\}. \quad (47)$$

Using next the equality [49]:

$$\mathcal{L}(1/2) = \frac{\pi}{4(\pi - 2)}, \quad (48)$$

we find that the right-hand-side of Eq.(47) attains the form

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

which expression coincides exactly with the earlier result obtained in Refs.[22] and [23] within the framework of a different, compared to ours, analytical techniques. The result in Eq.(49) 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 in hard-core lattice gases of arbitrary density [21], which supports in a way the validity of the approximation invoked in Eq.(8).

5 Conclusion

To conclude, we have studied analytically the intrinsic frictional properties of adsorbed monolayers, composed of mobile hard-core particles undergoing continuous exchanges with the vapor. 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 has been first introduced in Ref. [26] for a related model of a driven tracer particle dynamics in a one-dimensional lattice gas with conserved particles 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 have 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 have demonstrated next that in the limit of a vanishingly small external bias this relation attains a 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. Corresponding friction coefficient has been also 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-know result of Refs. [22] and [23] in the limit when the particles number is conserved.
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