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Dynamics of a driven probe molecule in a liquid monolayer

J. De Coninck[1], G. Oshanin[1] and M. Moreau[2]

[1] *Centre de Recherche en Modélisation Moléculaire, Service de Physique Statistique et Probabilités, Université de Mons-Hainaut - 20 Place du Parc, 7000 Mons, Belgium*

[2] *Laboratoire de Physique Théorique des Liquides, Université Paris VI*
4 Place Jussieu, 75252 Paris Cedex 05, France

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Abstract. – We study the dynamics of a probe molecule, driven by an external constant force in a liquid monolayer on top of a solid surface. In terms of a microscopic, mean-field–type approach, we calculate the terminal velocity of the probe molecule. This allows us to establish the analog of the Stokes formula, in which the friction coefficient is interpreted in terms of the microscopic parameters characterizing the system. We also determine the distribution of the monolayer particles as seen from the stationary moving probe molecule and estimate the self-diffusion coefficient for diffusion in a liquid monolayer.

Thin liquid films adsorbed on solid surfaces or confined in a narrow space between two solids represent a remarkable example of a two-phase physical system, in which an intrinsically disordered liquid phase is spanned by and contends with the ordering potential of the solid. It is well appreciated by now that the behaviour of such films is markedly different from the customary behaviour of the bulk liquids: experiments reveal effects of solid-like or glassy response to an external shear, sharp increase of relaxation times and of the films' viscosity [1]-[5]. The departure from the bulk behaviour is progressively more pronounced the thinner the film is and is interpreted usually as the manifestation of intricate cooperative effects, whose nature is not yet completely elucidated (see, *e.g.*, [2]).

In this letter we study cooperative behaviour in a liquid monolayer on solid surface, arising in response to internal perturbances created by a single probe molecule (say, a charge carrier), which is driven by constant external force. We propose here a simple analytically soluble model, which allows us to determine the stationary, non-homogeneous distribution of the monolayer particles as seen from the probe molecule and to derive a closed-form non-linear equation relating the terminal velocity of the probe to the magnitude of the driving force F. We find that in the limit of small F this equation reduces to the Stokes viscous-flow law, in which the friction coefficient ξ is determined explicitly, in terms of the microscopic parameters characterizing the system under study. We show that ξ combines the contributions of two different "dissipative" processes —temporary trapping of the probe by the potential wells, due to the interactions with

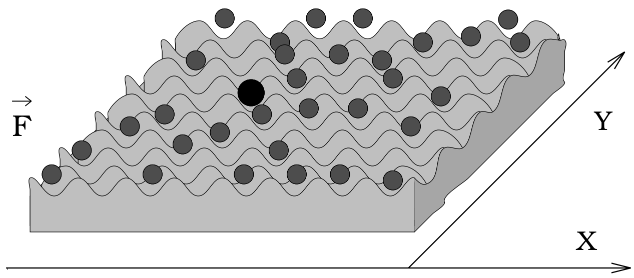

Fig. 1. – A schematic picture of a liquid monolayer on solid surface. The black circle denotes the probe molecule and smaller grey circles represent the monolayer particles. Wavy lines depict the wafer-like potential landscape created by the particle-solid interactions.

the solid atoms, and the cooperative effects associated with the formation of a non-homogeneous distribution of the monolayer particles around the probe. The knowledge of ξ also allows us to estimate the self-diffusion coefficient for diffusion in a liquid monolayer.

We start with the formulation of our model. Consider a 2D homogeneous monolayer of identical interacting particles moving randomly on top of an ideal crystalline surface (fig. 1). We suppose first that the particles' motion is induced by chaotic vibrations of the solid atoms. Second, we assume that the particle-particle interactions (PPI) are essentially weaker than the particle-solid interactions (PSI), so that the former do not perturb the wafer-like array of potential wells created due to the PSI (fig. 1). This permits us to adopt the conventional picture of the dynamics under such conditions (see [6] and references therein): the particles migration proceeds by thermally activated rare events of hopping from one well to another in its neighbourhood. The hopping events are separated by the time interval τ^*, which is the time a given particle typically spends in each well vibrating around its minimum; τ^* is related to the temperature β^{-1} and the barrier of the PSI by the Arrhenius formula. Further on, the PPI couple the dynamics of a given particle to motions of all others. That is, a particle escaping from a given well follows preferentially the gradient of the PPI potential (see, *e.g.*, [7], [8] for discussion). The realistic PPI are repulsive at short scales and show a weak, long-range attraction at longer interparticle separations. Here we simplify the actual behaviour by neglecting, first, the particle-particle attractions and, second, by approximating the repulsive part of the interaction potential by an abrupt hard wall, imposed at the distance equal to the interwell spacing. In such an idealized model the hopping probabilities are naturally decoupled from the particles distribution and all hopping directions are equally probable. The hard-core repulsion prevents multiple occupancy of any potential well —we suppose that a particle may hop into the target well only in the case when the latter is unoccupied at this moment of time; otherwise, the particle attempting to hop is repelled back to its position.

The key aspect in our model is the probe molecule (abbreviated as PM in the following), which is subject to an external constant (small) force F directed along the X-axis (fig. 1). We suppose that the PM also performs an activated hopping motion, constrained by the hard-core interactions with the monolayer particles. The typical time which the PM spends being trapped by each well is denoted as τ, which is dependent on the probe-solid interactions and hence may differ from τ^*. Varying τ, we can mimic different possible regimes. For instance, the choice $\tau = 0$ corresponds to the situation when the PM simply slides regardless of the surface corrugation. Now, in contrast to the monolayer particles the PM dynamics is anisotropic due to the applied force; that is, on escaping from the wells, the PM attempts to hop preferentially in the direction of F. Supposing for simplicity that the wells form a square (X, Y)-lattice of spacing σ, we define the probability $q(X,Y|X',Y')$ of an attempt to hop from the well at (X,Y) to the adjacent well at (X',Y') as

$$q(X,Y|X',Y') = Z^{-1}\exp[\beta F (X' - X)/2],\; Z = 4\cosh^2(\beta\sigma F/4)\,. \tag{1}$$

To take into account the hard-core repulsion between the PM and the monolayer particles, we stipulate that the PM hops into the target well only in the case when it is vacant at this moment of time. Otherwise, it remains at its position.

Let $P(X,Y)$ ($\rho(X,Y)$) denote the probability that at time t the PM (a monolayer particle) occupies the well with the coordinates (X,Y). To derive the closed-form equations describing the time evolution of these properties, we assume that correlations between the occupations of different wells decouple. It was shown recently in [9] that such a decoupling provides an adequate description of the driven particle dynamics in a one-dimensional symmetric hard-core lattice gas, in which case the hindering effect of the gas particles is much stronger than in 2D. We thus expect that in the 2D situation under study such an approach will yield the correct dependence of the PM terminal velocity on the system parameters; we do not expect, of course, to obtain exact numerical factors. Decoupling the correlations, we have

$$4\,\tau^*\frac{\mathrm{d}}{\mathrm{d}t}\rho(X,Y) = \sum_{(X',Y')}\{-(1-\rho(X',Y'))\,\rho(X,Y) + (1-\rho(X,Y))\,\rho(X',Y')\}, \tag{2}$$

which holds for all wells excluding the wells adjacent to the PM position. Next, we find

$$\begin{aligned}\tau\frac{\mathrm{d}}{\mathrm{d}t}P(X,Y) = \sum_{(X',Y')}\{&-q(X,Y|X',Y')\,P(X,Y)\,(1-\rho(X',Y')) + \\ &+ q(X',Y'|X,Y)\,(1-\rho(X,Y))\,P(X',Y')\}\,.\end{aligned} \tag{3}$$

The sum in eqs. (2) and (3) runs over all wells (X',Y') adjacent to the well at position (X,Y).

Multiplying both sides of (3) by X and summing over all wells, we obtain

$$\begin{aligned}V &= \frac{\sigma}{\tau}(q_+ - q_-) - \frac{\sigma}{\tau}\sum_{X,Y}P(X,Y)\,(q_+\,\rho(X+\sigma,Y) - q_-\,\rho(X-\sigma,Y)) = \\ &= \frac{\sigma}{\tau}[q_+\,(1 - f_V(\lambda_1=\sigma,\lambda_2=0)) - q_-\,(1 - f_V(\lambda_1=-\sigma,\lambda_2=0))],\end{aligned} \tag{4}$$

where V is the X-component of the PM velocity, $q_\pm = \exp[\pm\beta\sigma F/2]/Z$ and $f_V(\lambda_1,\lambda_2)$ denotes the time-dependent probe-particle correlation function; the subscript "V" signifies that this property is itself dependent on the PM velocity.

The dynamics of $f_V(\lambda_1,\lambda_2)$ is a superposition of two different processes —the particles diffusion and the motion of the PM. From eqs. (2) and (3) we find that in the continuous-space limit $f_V(\lambda_1,\lambda_2)$ obeys (see [9] for details of derivation in the 1D case)

$$\frac{\partial}{\partial t}f_V(\lambda_1,\lambda_2) = D^*\left(\frac{\partial^2}{\partial\lambda_1^2}+\frac{\partial^2}{\partial\lambda_2^2}\right)f_V(\lambda_1,\lambda_2) + V\frac{\partial}{\partial\lambda_1}f_V(\lambda_1,\lambda_2), \tag{5}$$

where $D^* = \sigma^2/4\tau^*$ is the "bare" diffusion coefficient of an isolated particle.

Let us discuss now the initial and boundary conditions to eq. (5). First, we suppose

$$f_V(\lambda_1,\lambda_2)|_{\lambda_1,\lambda_2\to\pm\infty} = f_V(\lambda_1,\lambda_2)|_{t=0} = \rho, \tag{6}$$

which means that correlations between $P(X,Y;t)$ and $\rho(X+\lambda_1,Y+\lambda_2)$ vanish in the limit $\lambda_1,\lambda_2\to\pm\infty$ and that initially the particles were uniformly distributed in the potential wells with mean density ρ. Another set of four equations can be derived by analyzing the evolution of $f_V(\lambda_1, \lambda_2)$ in the wells adjacent to the PM position (see for more details [9]). This gives the zero-flux boundary condition for $\lambda_1 = 0, \lambda_2 = \pm\sigma$ and

$$\frac{\partial}{\partial \lambda_1} f_V(\lambda_1, 0)\Big|_{\lambda_1 = \pm\sigma} = -\frac{V}{D^*} f_V(\pm\sigma, 0). \tag{7}$$

The solution of the mixed boundary value problem in eqs. (5) to (7) yields the following result for the particle distribution around the stationary moving PM:

$$f_V(\lambda_1, \lambda_2) = \rho + 2\rho \exp\left[-\frac{P\lambda_1}{\sigma}\right]\left\{\frac{\cosh(P) - 2S_-}{S_+ + 2S_-} \sum_{n=-\infty}^{\infty} \frac{I'_{2n}(P)}{K'_{2n}(P)} T_{2n}\left(\frac{\lambda_1}{r}\right) K_{2n}\left(\frac{Pr}{\sigma}\right) - \right.$$
$$\left. - 2\left(1 + \frac{\cosh(P) - 2S_-}{4(S_+ + 2S_-)}\right) \sum_{n=1}^{\infty} \frac{I_{2n-1}(P)}{K_{2n-1}(P)} T_{2n-1}\left(\frac{\lambda_1}{\mathrm{r}}\right) K_{2n-1}\left(\frac{Pr}{\sigma}\right)\right\}, \tag{8}$$

where $S_\pm$ are given by

$$S_+ = -\sum_{n=-\infty}^{\infty} \frac{I'_{2n}(P)}{\{\ln[K_{2n}(P)]\}'} \quad \text{and} \quad S_- = \sum_{n=1}^{\infty} I_{2n-1}(P)\{\ln[K_{2n-1}(P)]\}'. \tag{9}$$

In eqs. (8) and (9) P is the "Peclet number", $P = V_\infty \sigma/2D^*$, V_∞ is the PM terminal velocity, the prime stands for the derivative with respect to P, $r = \sqrt{\lambda_1^2 + \lambda_2^2}$, while $K_n(x)$, $I_n(x)$ and $T_n(z)$ denote the modified Bessel functions and the Tchebyscheff polynomials, respectively. Inserting eqs. (8) and (9) into eq. (4), we arrive at an equation closed with respect to V_∞. This non-linear transcendental equation is not analytically soluble, and we will thus seek an approximate solution, assuming that V_∞ is sufficiently small, such that $P < 1$. Expanding $f_V(\pm\sigma, 0)$ to the second order in powers of P, we obtain

$$V_\infty \approx \frac{(q_+ - q_-)(1 - \rho)}{(\tau/\sigma) + (q_+ + q_-)\sigma\rho/D^*} \times$$
$$\times \left[1 + \frac{2\rho}{1-\rho}\left(\frac{(q_+ - q_-)(1-\rho)\sigma^2}{2D^*\tau + 2(q_+ + q_-)\rho}\right)^2 \left\{\ln\left(\frac{(q_+ - q_-)(1-\rho)\sigma^2}{2D^*\tau + 2(q_+ + q_-)\rho}\right) + \gamma + 1/2\right\}\right], \tag{10}$$

where $\gamma = 0.577\ldots$ is the Euler constant. Now, several comments on the result in eq. (10) are in order. We find, first, that $P < 1$ and our approximation is justified when the inequality $(q_+ - q_-)(1-\rho)\sigma^2 < 2D^*\tau + 2(q_+ + q_-)\sigma^2\rho$ is fulfilled. This happens, namely, in the case when the applied force is sufficiently small, or when either $\rho > 1/3$, or $D^*\tau/\sigma^2 > 1$. We note also that in the limit $P < 1$ the second term in brackets in eq. (10) is much smaller than unity and can be safely neglected. Further on, eq. (10) shows that the PM velocity is controlled by the combination of two different factors —trapping by the wells and the hindering effect of the monolayer particles. The first factor dominates in the limit when $D^*\tau/\sigma^2 \gg \rho$, a behaviour which may take place in the case when the barrier of the probe-solid interactions is much stronger than that for the PSI. In this limit eq. (10) reduces to the essentially mean-field result $V_\infty \approx (q_+ - q_-)\sigma/\tau_\omega$, where $\tau_\omega = \tau/(1-\rho)$. We remark that since τ is appropriate for the motion in the stagnant layer, rather than in the bulk phase, we may expect that even in this limit of the well-stirred monolayer the terminal velocity V_∞ will be much less than the corresponding (to this value of F) velocity in the bulk liquid. Next, the prevalence of the cooperative effects appears in the limit when the ratio $D^*\tau/\sigma^2$ is less than ρ. Here we have $V_\infty \approx (q_+ - q_-)(1-\rho)D^*/\sigma\rho$, *i.e.* the terminal velocity is proportional to the "bare" diffusion constant of the monolayer particles and vanishes when $D^* \to 0$. This means that the particles have to diffuse away of the PM in order that it can move. As a matter of fact, such a dependence mirrors an even stronger effect: the monolayer particles, whose motion is random with no preferential direction, accumulate in front of the obstacle (the PM), which moves at a constant velocity.

Next, using the notations of eq. (1) and supposing that $\beta\sigma F \ll 1$, we cast eq. (10) into the following physically revealing form:

$$F = \xi\, V_\infty, \ \xi = \frac{2}{(1-\rho)\sigma\beta} \left(\frac{2\tau}{\sigma} + \frac{\sigma\rho}{D^*}\right), \tag{11}$$

which can be thought of as the analog of the Stokes formula for the system under study; the friction coefficient ξ is expressed through the microscopic parameters and displays the combined hindering effect of the potential wells and of the monolayer particles on the PM dynamics. The friction coefficient is proportional to τ, which is related to the probe-solid interactions, and diverges when either $D^* \to 0$ or $\rho \to 1$.

Further on, from the Einstein relation between the mobility and the diffusivity of a test particle (the PM) we find

$$D_{\rm PM} = \frac{(1-\rho)\, D\, D^*}{D^* + 2\,\rho\, D}, \tag{12}$$

where $D = \sigma^2/4\tau$ and $D_{\rm PM}$ are the PM "bare" and self-diffusion coefficients, respectively.

Let us now briefly discuss the density distribution of the monolayer particles as seen from the stationary moving PM. The local density in the nearest to the PM wells $f_V(\pm\sigma, 0) \approx \rho(1 \pm V_\infty\sigma/D^*)$, *i.e.* in front of (past) the PM the local density exceeds (is less than) the average density of the monolayer particles. Further on, at large separations of the PM, such that $\lambda_1 \gg \Lambda = D^*/V_\infty$, the density profile is characterized by

$$f_V(\lambda_1, 0) \approx \rho \left(1 + \left(\frac{\sigma}{\Lambda}\right)^2 \left(\frac{\pi\Lambda}{\lambda_1}\right)^{1/2} \exp[-\lambda_1/\Lambda]\right), \tag{13}$$

which means that the excess density in front of the PM vanishes exponentially with the distance. The parameter Λ can be identified as the characteristic length of the condensed region in front of the PM. We note, however, that this parameter is not very informative; particularly, it diverges when either $D^* \to \infty$ or $\rho \to 1$, which is a bit misleading since in this limit the excess density tends to zero, *i.e.* the monolayer is homogeneous. A better parameter is the integral excess density Ω along the λ_1-axis,

$$\Omega = \int_\sigma^\infty {\rm d}\lambda_1\, (f_V(\lambda_1, 0) - \rho) \approx \frac{(q_+ - q_-)\rho(1-\rho)\sigma^3}{D^*\tau + (q_+ + q_-)\sigma^2\rho} \{-\ln(P/2) + 1 - \gamma\}. \tag{14}$$

Equation (14) shows that the condensed region is actually absent when either $\rho \to 1$ or $D^* \to \infty$ and increases when the driving force is increased. We also remark that when the parameter $D^*\tau/\sigma^2$ is sufficiently large, Ω is a non-monotoneous function of ρ.

Finally, we find that at large distances past the PM the density follows

$$f_V(\lambda_1, 0) \approx \rho \left(1 + \frac{1}{8} \left(\frac{\sigma}{\Lambda}\right)^4 \left(\frac{\pi\Lambda}{|\lambda_1|}\right)^{1/2}\right), \ |\lambda_1| \gg \Lambda. \tag{15}$$

Equation (15) displays two remarkable features: First, the particle density past the PM approaches its average value only as a power law, which mirrors strong memory effects of the medium and signifies that diffusive homogenization of the monolayer, constrained by the hard-core interactions, is a very slow process. Second, it shows that the density is a non-monotonous function of λ_1; $f_V(\lambda_1 = -\sigma, 0) < \rho$ and approaches ρ from above when $\lambda_1 \to -\infty$.

To summarize, we have studied the dynamics of a probe molecule driven by an external constant force in a 2D monolayer of particles moving randomly on top of a solid surface. We have proposed a microscopic model description of such a system evolution and calculated the PM terminal velocity V_∞, the self-diffusion coefficient D_{PM} and the stationary distribution of the monolayer particles as seen from the probe molecule. We have shown that this distribution is strongly asymmetric: Past the PM, the local density is lower than the average density ρ and tends to ρ as a power law of the distance, revealing strong memory effects of the medium. In front of the PM the density is higher than the average —the monolayer particles accumulate in front of the PM, creating a sort of "traffic jam" which impedes its motion. We show that the PM terminal velocity is controlled by the size of the jammed region, which is, in turn, dependent on the driving force, as well as on the density of the monolayer and on the rate at which the monolayer particles may diffuse away from the PM. The balance between the driving force and the rate of the monolayer homogenization manifests itself as a medium-induced frictional force exerted on the PM, which shows a viscous-like behaviour for small driving forces. This resembles in a way the situation described in [10], which considered the dynamics of a single charged particle moving at a constant velocity above the surface of a dielectric fluid. Here the cooperative behaviour emerges because of the electrostatic interactions between the particle and the fluid molecules. The particle perturbs the fluid surface creating a "bump", which travels together with the particle increasing effectively its mass and thus producing a frictional drag force exerted on the particle.

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