Diffusion on a solid surface: Anomalous is normal

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We present a numerical study of classical particles diffusing on a solid surface. The particles’ motion is modeled by an underdamped Langevin equation with ordinary thermal noise. The particle-surface interaction is described by a periodic or a random two dimensional potential. The model leads to a rich variety of different transport regimes, some of which correspond to anomalous diffusion such as has recently been observed in experiments and Monte Carlo simulations. We show that this anomalous behavior is controlled by the friction coefficient, and stress that it emerges naturally in a system described by ordinary canonical Maxwell-Boltzmann statistics.

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Diffusion of atoms, molecules, and clusters on solid surfaces occurs in a number of modern technologies involving self-assembled molecular film growth, catalysis, and surface-bound nanostructures. The study of the motion of small and large organic molecules, and of adsorbed metal clusters composed of tens and even hundreds of atoms, has led to the unexpected observation that, as with single atoms, long jumps may play a dominant role in these motions.

Theoretical, numerical, and phenomenological discussions of surface diffusion have led to the clear understanding that jumps beyond nearest neighbors are ubiquitous in some parameter regimes. However, these studies focus on the fact that the motion is necessarily diffusive (which is the case at very long time scales). The possibility that jumps can be so long as to lead to superdiffusive motion over appreciable intermediate time scales is recognized as an interesting problem, but one in which Lévy walks or flights are invoked as a model input. Although Lévy-walk-like behavior is clearly observed in Hamiltonian systems and in microcanonical simulations, it is generally believed that such a fine signature of chaos is fully smeared away by thermal fluctuations. In the work we show that Lévy-like statistics appear quite naturally over long time scales within the usual Langevin framework for underdamped motion in a periodic or a random potential.

While a detailed analysis of surface diffusion requires extensive calculations (e.g., ab initio, or molecular dynamics), even the most powerful currently available computers can not carry such calculations to anywhere near experimentally relevant time scales. Moreover, current experimental probes of the topography of surfaces, scanning tunneling microscopy and atomic force microscopy, are usually carried out at relatively high temperatures, which leads to additional difficulties for first-principles calculations. Therefore, simpler approaches are essential and valuable.

We consider a generic model of classical particles moving in a two-dimensional potential, under the action of thermal fluctuations and dissipation, the important control parameter being the friction coefficient. In spite of the simplicity of the model, we find that it is able to reproduce the entire range of experimentally and computationally observed phenomena, from superdiffusion all the way to subdiffusion.

The equation of motion of a particle of mass m on the surface is

\[ m\ddot{x} = -\nabla V(x/\lambda) - \mu \dot{x} + \xi(t) \] (1)

where \( \lambda \) is the characteristic length scale of the potential. The parameter \( \mu \) is the coefficient of friction, and the \( \xi(t) \) are mutually uncorrelated white noises that obey the fluctuation-dissipation relation \( \langle \xi(t)\xi(t') \rangle = 2\mu k_B T \delta(t-t') \). We first consider the nonseparable periodic potential

\[ V(x, y) = V_0 \cos \left( \frac{\pi x}{\lambda} + \frac{\pi y}{\lambda} \right) \cos \left( \frac{\pi x}{\lambda} - \frac{\pi y}{\lambda} \right) \] (2)

where \( V_0 \) is the barrier height at the saddle points.

Equation (1) can be rewritten in scaled dimensionless variables, \( r_x = x/\lambda, r_y = y/\lambda, \) and \( s = \sqrt{V_0/m\lambda^2} \), leaving only two independent parameters, the scaled temperature \( T \) and the scaled dissipation \( \gamma \),

\[ T = k_B T/V_0, \quad \gamma = \mu \lambda/\sqrt{mV_0}. \] (3)

We study four properties of the motion of the particle: the mean square displacement, the dependence of the diffusion coefficient on friction, the probability density function of displacements, and the velocity power spectrum.

Normal diffusive behavior is characterized by a linear time dependence of the mean square displacement,
\[ \langle r^2(s) \rangle \sim s. \] Non-diffusive behavior shows a different time dependence, \[ \langle r^2(s) \rangle \sim s^{\alpha}, \text{ with } \alpha > 1 (< 1) \] for superdiffusive (subdiffusive) motion. In Fig. 1 we show typical trajectories obtained for two friction coefficients upon numerical simulation of the equations of motion with \( T = 0.2 \) (we use this value throughout). One (left panel) is for a large friction coefficient, and the particle follows typical diffusive motion characterized by short steps of length \( \sim \lambda \) and frequent changes in direction. The other (right panel) corresponds to a small friction coefficient and clearly shows the preponderance of long trajectories obtained for two friction coefficients.

FIG. 1: Left: A trajectory for \( \gamma = 1 \) over \( t = 20,000 \) time units. Right: A trajectory for \( \gamma = 0.04 \) over \( t = 15,000 \) time units. The period of the potential is \( \lambda = 4 \). Note the different scales in the two panels.

The evolution of \( \langle r^2 \rangle \) averaged over 1000 particles is shown in Fig. 2 for several friction coefficients. For very long times the motion is diffusive, as expected, but for small \( \gamma \) and at intermediate times there is clear superdiffusive ballistic (\( \alpha = 2 \)) behavior over several decades in time. This is reflective of the long straight stretches seen in the low-\( \gamma \) trajectory in Fig. 1. We stress that this behavior has emerged naturally and has not required explicit insertion of any but ordinary thermal fluctuations in the model.

Even though the motion of the particle may include long superdiffusive stretches, at long times the motion is necessarily diffusive. The dependence of the diffusion coefficient on the friction for small and large \( \gamma \) can be obtained analytically using the approximate relation \( D \approx \langle l^2 \rangle / 2\tau \), where \( \langle l^2 \rangle \) is the mean square size of a jump out of one well and into another, and \( \tau^{-1} \) is the mean jump rate (related to the familiar “mean escape rate”). In the overdamped regime, jumps typically occur from one well to a neighboring well, so \( \langle l^2 \rangle \approx 1 \). Familiar Kramers formulas can be used to obtain the mean escape rate \[ \tau \sim \frac{1}{2\pi} \left( \sqrt{\frac{\gamma^2}{4} + 2\pi^2 - \frac{\gamma}{2}} \right) e^{-\frac{\gamma}{2}} \sim \frac{\pi}{\gamma} e^{-\frac{\gamma}{2}}. \]

FIG. 2: \( \langle r^2 \rangle / 4s \) for a particle in the periodic potential, for \( \gamma = 0.0004 \) (solid), 0.004 (dotted), 0.04 (dashed) and 0.4 (dot-dashed). The straight-line segment has unit slope as a guide to the eye. Inset: Diffusion coefficient as a function of \( \gamma \). The solid lines correspond to the theoretical calculations (Eqs. 4-6).

The \( \gamma^{-1} \) dependence of \( D \) arises because \( \langle l^2 \rangle \) is independent of \( \gamma \) while \( \tau \sim \gamma \). In the underdamped limit,

\[ D \sim \frac{\pi T}{4\gamma} e^{-\frac{\gamma}{4\gamma}}, \] (5)

that is, again an inverse dependence on friction. The theoretical diffusion coefficient as a function of the friction parameter is shown as the solid curves in the inset of Fig. 2. The symbols are the simulation results. The \( \gamma^{-1} \) dependences have been noted in the literature, but we have provided explicit forms with no adjustable parameters.

The diffusion coefficient characterizes only the very
long time asymptotic dynamics. The interesting intermediate dynamics in the low friction regime that gives rise to long stretches of ballistic motion is reflected in the probability distribution function (pdf) of particle displacements $r$. This pdf is shown in Fig. 3 for $\gamma = 0.0004$ and tree different time intervals $\tau_s$. For comparison, we also show a typical pdf for high damping ($\gamma = 1$) at the intermediate time interval. In the high-$\gamma$ curve the highest maximum corresponds to no jumps (by far the most likely event at short times). The next is associated with jumps to a nearest neighbor well, and so on. In contrast, the low-$\gamma$ curves show a very different behavior, with features strongly resembling those of a Lévy-walk model: a peak at small displacements, a power-law intermediate regime, and a side hump at high displacements. Each of these is a distinct signature of Lévy-walk-like dynamics, but one must be cautious in the detailed interpretation of these components. The persistent small displacement peak is associated with long trapping periods during which a particle does not move at all because its energy is not sufficient to overcome the barrier. The high displacement peak, which moves outward with velocity of order unity, is associated with ballistic motion of those particles that acquire enough energy to move (and lose it very slowly). Genuine Lévy-walk dynamics also exhibit a low displacement peak and a superdiffusive peak separated by a power law behavior, but there are some important differences. First, our distribution reflects ballistic transport in the intermediate regime (in the language of Ref. [15], ballistic transport occurs when $0 < \alpha < 1$ in the Lévy model), whereas the regime where the Lévy model shows the features we have described is associated with sub-ballistic (but still superdiffusive) behavior (again, in the language of Ref. [15], the behavior when $1 < \alpha < 2$). Second, the slope in our power law regime (approximately 0.7) is not related to the exponent $\alpha$ in the mean square displacement as it is for the Lévy walk (where the slope is $4 - \alpha$). Third, our side hump is strongly broadened whereas the side hump in the Lévy-walk model is associated with motion at a single constant velocity. In our case the velocity varies according to the equilibrium Maxwell-Boltzmann distribution. Nevertheless, the qualitative features of our distribution track those of the Lévy walk. Note that the existence of the pronounced side hump reflects the fact that the particles performing long steps ("flights") are those with a velocity in the tail of the Maxwellian distribution.

Long ballistic excursions imply velocity correlations over considerable time intervals. The velocity power spectrum $S(\omega) = \langle V(\omega)V(-\omega) \rangle$ for different values of $\gamma$ is shown in Fig. 4. The pronounced peak at $\omega_0 = \pi \sqrt{2}$ is associated with small oscillations in one well. At lower frequencies, $\omega \ll \omega_0$, one observes a power-law growth of $S(\omega)$ that corresponds to the persistent time correlations associated with the ballistic excursions. At even smaller frequencies there is a crossover to $S(\omega) = \text{const} \propto D$, indicating full decorrelation and pure diffusion.

Disorder in surfaces occurs due to the presence of vacancies and other defects. We have generated a random potential surface described by a Gaussian distribution with a correlation function $V(x) = (\varepsilon / 2\pi \lambda^2) \exp(-|x|^2 / 2\lambda^2)$ (see [16, 17, 18, 19] for details). We set the intensity $\varepsilon = 100$ and the characteristic length $\lambda = 4$ in our simulations. A typical surface generated with this algorithm whose average height $V_0$ equals that of the periodic potential is shown in Fig. 5.

The exponent $\alpha$ in $\langle r^2(s) \rangle \sim s^\alpha$ at intermediate times shows the entire range of behaviors from subdiffusive to superdiffusive with changing friction. In Fig. 6 we show $\langle r^2(s) \rangle / 4s$, averaged over 5000 particles, as a function of time, for several values of $\gamma$. In the overdamped regime we clearly observe subdiffusive behavior ($\alpha < 1$), while superdiffusive ($\alpha > 1$) behavior is seen for very small $\gamma$. The exponents $\alpha$, calculated over the last decade of the time variation of the mean square displacement within our finite simulation times, are plotted in the inset of Fig. 6 as a function of $\gamma$. Although the subdiffusive behavior is probably the true asymptotic behavior in the
underdamped regime, the motion of the particle includes a ballistic range that can extend over many decades of time. The pdf of the particle’s displacements under these conditions shows a structure strongly resembling one for Lévy walks. This may explain a number of observations involving superdiffusive motion of organic molecules and atomic clusters on surfaces without the need to invoke extraordinary fluctuations beyond the usual thermal description. The long-time behavior is diffusive in all cases, and we have been able to predict theoretically the dependence of the diffusion coefficient on friction over essentially the entire range of values of the friction parameter with no adjustable parameters. The situation in a random potential is even more complex, and exhibits a wide range of subdiffusive to superdiffusive regimes. Further analysis of the random potential case, and a more extensive presentation of the periodic problem, will be detailed elsewhere.

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