Unsolved Problems of Surface Diffusion at Low Friction

Katja Lindenberg*, A. M. Lacasta†, J. M. Sancho** and A. H. Romero‡

*Department of Chemistry and Biochemistry 0340, and Institute for Nonlinear Science, University of California, San Diego, La Jolla, California 92093-0340, USA
†Departament de Física Aplicada, Universitat Politècnica de Catalunya, Avinguda Doctor Marañon 44, E-08028 Barcelona, Spain
**Departament d'Estructura i Constituents de la Matèria, Facultat de Física, Universitat de Barcelona, Diagonal 647, E-08028 Barcelona, Spain
‡Cinvestav-Queretaro, Libramiento Norponiente No 2000, Real de Juriquilla, 76230 Queretaro, Qro, Mexico

Abstract. Surface transport and diffusion at low damping reveals a number of unexplained or at least not systematically explained behaviors. Here we present two problems that require further study for a full understanding. One involves motion on a random surface, the unresolved issue being the parameter regimes leading to subdiffusive, diffusive, and superdiffusive motions at intermediate times. The other involves the temperature dependence of maximal diffusion on a periodic surface in the presence of a constant external force.

Keywords: Friction, Surfaces, Langevin equation, Superdiffusion
PACS: 05.40.-a,68.35.Fx,68.43.Jk

INTRODUCTION

Transport and diffusion of atoms, molecules, molecular clusters, and colloidal particles on periodic or random surfaces continues to be a problem of ubiquitous interest because there are constantly new and technologically important experiments that involve such motions, and because there are still many unanswered theoretical issues associated with these problems in spite of their long history ([1, 2, 3, 4, 5, 6] and extensive references therein). This being a volume associated with a conference on unsolved problems involving noise, we focus on some transport and diffusion problems on surfaces that lead to as yet unresolved issues.

Theoretical analyses of the motion of particles on surfaces would ideally rely on *ab initio* or molecular dynamics models in which the particles and the surfaces are represented in their full microscopic detail. This is as yet impossible over experimentally relevant time scales. A compromise is to rely on mesoscopic phenomenological paradigms in which one focuses on a few dynamical variables that describe the particle of interest. Its interaction with the surface is represented by a surface potential, a frictional force, and a stochastic component to represent thermal effects and other degrees of freedom not microscopically considered. External forces for the study of transport processes can also be included.

Among the mesoscopic models of choice in the longevous history of the subject are *overdamped* Langevin equations. The generic form for such models to describe the

CP800, *Unsolved Problems of Noise and Fluctuations: UPoN 2005*
edited by L. Reggiani, C. Pennetta, V. Akimov, E. Alfinito, and M. Rosini

evolution of a dynamical variable $x(t)$ (e.g. the displacement of a particle in a one-dimensional system) would be $\gamma\dot{x} = -V'(x) + \xi(t) + F(x,t)$, where a dot denotes a derivative with respect to time t, a prime is a derivative with respect to the argument, $\xi(t)$ is δ-correlated Gaussian noise, $\langle \xi_i(t)\xi_j(t')\rangle = 2\gamma k_B T \delta_{ij}\delta(t-t')$ where T is the temperature, and $F(x,t)$ is an external force. The damping coefficient γ is usually not written explicitly as we have done because one can of course simply divide through by it. The equation represents an overdamped system because it is missing the inertial contribution proportional to $\ddot{x}$ that would appear in Newton's Law. The associated model of choice on a discrete lattice is a nearest neighbor random walk, and the probabilistic description based on the density $P(x,t)$ that the particle is at x at time t is the Fokker-Planck equation. The equation with full inertial contributions from which the overdamped equation emerges in the large γ limit is $m\ddot{x} = -\gamma\dot{x} - V'(x) + \xi(t) + F(x,t)$, where m is the particle mass (set to unity henceforth). This equation is not analyzed nearly as often as is the overdamped case because the second time derivative seriously complicates the mathematics.

The overdamped model and its discrete counterpart (and its higher dimensional versions) are of course not able to reproduce all observations, especially those that can not be described as one would a nearest neighbor random walk or simple diffusion in a potential. This has long been recognized, and extensions of the models have been the subject of an extensive literature. A few examples involve the extension of random walk models to include jumps to neighbors beyond the nearest (and even to very distant ones), persistent behavior that causes a particle to preferentially continue jumping along a previously chosen direction, and the generalization of $\xi(t)$ to non-white and/or non-Gaussian noise. In recent years there have been a number of experimental observations of particles on surfaces that seem to move over long distances in one direction before moving in another (see references in [3]), and a number of these generalizations have been invoked in an attempt to explain the observations. It is our thesis that many of these observations do not require special modeling of the noise or other memory effects, but can be explained by including the inertial contribution and exploring the small-γ regime.

In the course of these investigations, we have encountered some results that lead to open questions to be explored, and here we exhibit two of them. One is related to the nature of the diffusive process on random surfaces in the absence of external forces, and will be presented in the next Section. The other concerns a temperature dependence in the diffusion on periodic surfaces in the presence of a constant external force. This will be presented in the subsequent Section. We close with a brief summary.

SUPERDIFFUSION?

We consider a two-dimensional surface in the absence of external forces. In conveniently scaled variables the equations are (with independent noises in different directions)

$$\begin{aligned} \ddot{x} &= -\gamma\dot{x} - \frac{\partial}{\partial x}V(x,y) + \xi_x(t), \\ \ddot{y} &= -\gamma\dot{y} - \frac{\partial}{\partial y}V(x,y) + \xi_y(t), \end{aligned} \qquad (1)$$

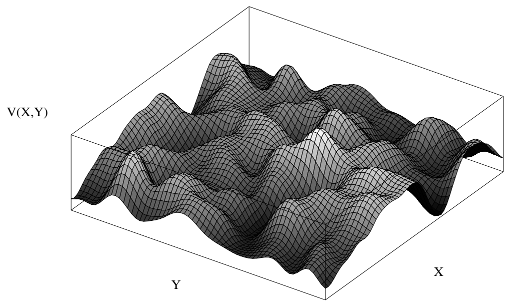

FIGURE 1. Typical random potential.

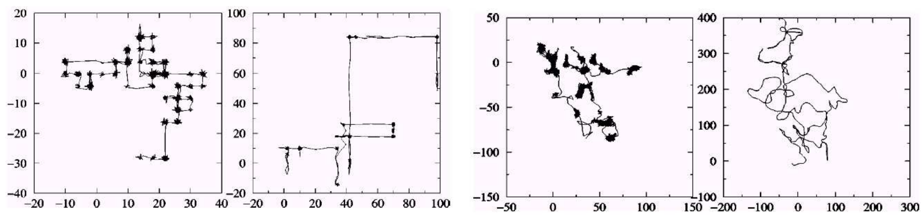

FIGURE 2. Left two panels: typical trajectories for high damping (far left) and low damping (second from left) on a periodic lattice. Right two panels: typical trajectories for high damping (second from right) and low damping (far right) on a random lattice. The average potential heights is the same for both lattices. For detailed parameter values see [3].

where the potential $V(x,y)$ is either periodic or random [2, 3]. If random, it is characterized by a distribution, which we choose to be a Gaussian, with a correlation function that we choose to be exponential, $\langle V(\mathbf{x})V(\mathbf{x}')\rangle = g(\mathbf{x}-\mathbf{x}')$ with

$$g(\mathbf{x}-\mathbf{x}') = \frac{\varepsilon}{2\pi\lambda^2} e^{-|\mathbf{x}-\mathbf{x}'|^2/2\lambda^2}, \tag{2}$$

and $\mathbf{x} = (x,y)$, $\mathbf{x}' = (x',y')$. The correlation function is parameterized by the intensity ε (specified in terms of the temperature) and the characteristic length λ (we set $\lambda = 4$ in our simulations). In Fig. 1 we show a small portion of such a random potential. In Fig. 2 we show typical trajectories for high and low damping, both for a periodic potential (for comparison) and for a random potential. The situation of interest here is that of the rightmost panel in the figure.

In a periodic potential we have shown that, for a fixed set of potential parameters and temperature, the motion ranges from diffusive to superdiffusive over many intermediate decades of time as one lowers the damping [2, 3]. That is, the motion over many decades of time at sufficiently low damping is characterized by a mean square displacement

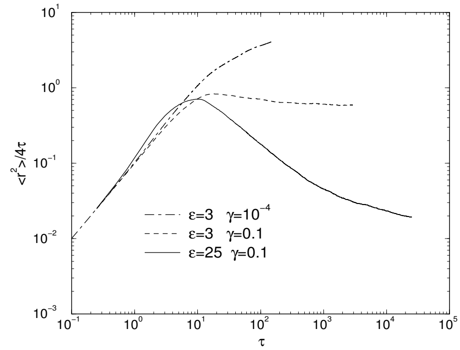

FIGURE 3. $\langle r^2 \rangle / 4\tau$ for three sets of values of the random potential intensity parameter ε and the damping coefficient γ as defined in [2, 3, 7].

proportional to t^α with $1 < \alpha \leq 2$ (at asymptotic times the motion becomes diffusive, that is, $\alpha \to 1$). We analyzed this motion in further detail and showed that the probability distribution function $P(r, \tau)$ of particle displacements r at time τ in the intermediate time regime shows many characteristics typical of Lévy walks. We stress that this behavior is caused entirely by inertial effects that become increasingly important as damping decreases, since the fluctuations in the model are white and Gaussian.

In a random potential we conjecture that the possible range of behaviors extends all the way from subdiffusive ($\alpha < 1$) to diffusive and superdiffusive [2, 3, 7]. It is fairly easy and not surprising to find parameter values that lead to subdiffusive behavior, since particles may get trapped for very long time intervals in extremely deep potential wells from which it is difficult to emerge [7, 8]. It is also fairly easy to find parameters that lead to diffusive behavior. The uncertain issue (*unsolved problem*) is the question of occurrence, parameter range, and time range of superdiffusion, which is associated with long open pathways that can occur with some probability in a random system. While we have not found a systematic set of parameter values such that the variation of a single parameter (e.g. damping) takes one through the subdiffusive-diffusive-superdiffusive behaviors, we have observed all three behaviors [7], as shown in Fig. 3.

TEMPERATURE DEPENDENCE

Our second *unsolved problem* deals with a particular temperature dependence in the case of transport over a *periodic* surface subject to a constant external force. The potential in suitably scaled units now is (again, in our simulations we set $\lambda = 4$)

$$V(x,y) = \frac{1}{2}\left[\cos\left(\frac{2\pi x}{\lambda}\right) + \cos\left(\frac{2\pi y}{\lambda}\right)\right]. \tag{3}$$

A constant force F_0 is applied along the x direction. We have explored the dependence of the mean velocity $v \equiv \lim_{t\to\infty}(\langle x(t)\rangle / t)$ and the diffusion coefficient $D \equiv$

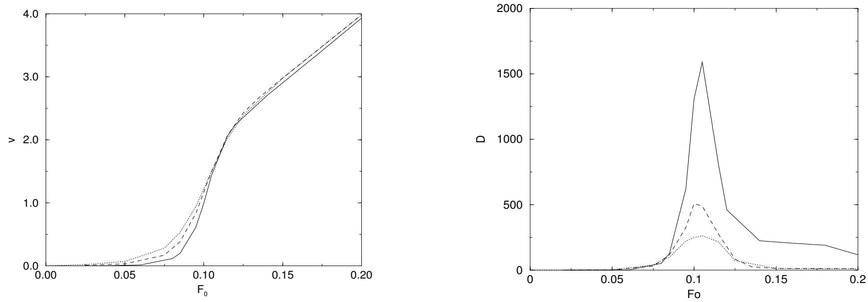

FIGURE 4. Mean velocity (left panel) and diffusion coefficient (right panel) vs F_0 for three values of the temperature: $\varepsilon = 0.15$ (solid curve), $\varepsilon = 0.20$ (dashed curve), and $\varepsilon = 0.25$ (dotted curve). The friction coefficient is fixed at $\gamma = 0.05$.

$\lim_{t\to\infty}(\langle[x(t)-\langle x(t)\rangle]^2/2t)$ on damping, force, and temperature [4]. The unexplained behavior concerns the behavior observed in Fig. 4.

In the left panel we present the velocity vs F_0 curves for three values of the temperature for a system with friction coefficient $\gamma = 0.05$. The panel on the right shows the associated diffusion coefficient for each of the three temperatures. The transition behavior observed in the velocity has been discussed in [4], and the principal effect of lowering the temperature is to sharpen the transition region, essentially without moving its location F_c ($F_c \sim 0.1$ for $\gamma = 0.05$). However, the effect on the diffusion coefficient is far more pronounced. While the location F_c of the peak is essentially temperature independent, the peak *grows* with *decreasing* temperature, that is, diffusion is *stronger* as temperature decreases. This behavior is consistent with a transition between locked and running states, as described in [4].

A plot of the maximum diffusion as a function of the temperature reveals the strongly nonlinear dependence

$$D_{max} \sim T^{-3.5}, \tag{4}$$

that is, the diffusion coefficient seems to grow without bound as temperature is lowered (in the overdamped system one finds that $D_{max} \sim T^{1/3}$ [4]). An interesting scaling behavior is observed if we plot the product $\varepsilon^{3.5}D$ as a function of $(F_0 - F_c)/\varepsilon^{1.5}$, as done in Fig. 5. With this scaling, all the curves in the right panel of Fig. 4 collapse onto the same curve. We stress that the exponents 3.5 and 1.5 of ε are simply numerical fits (and not necessarily the very best ones at that), although the divergent increase of D with decreasing temperature is supported by the simulations for the temperatures studied. In any case, the result (4) as well as the scaling behavior in Fig. 5 (or ones with even more accurate exponents) are the theoretically *unsolved problems* of this section.

SUMMARY

We have presented two unsolved problems involving noise. Both have to do with diffusion on surfaces when damping is low. One concerns motion over a random surface:

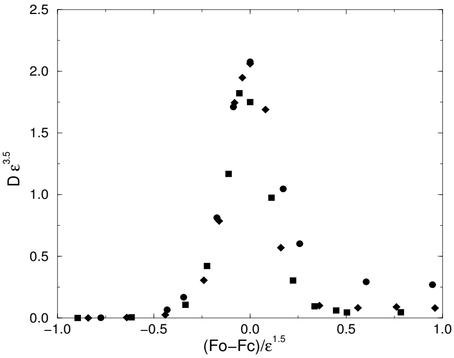

FIGURE 5. Scaled diffusion for $\gamma = 0.05$ for various temperatures. Dots: $\varepsilon = 0.15$; squares: $\varepsilon = 0.21$; diamonds: $\varepsilon = 0.25$.

while it is apparent that the motion may be subdiffusive, diffusive, or superdiffusive at intermediate times for appropriate parameter values, there is as yet no systematic understanding of the conditions that lead to each of these behaviors. The other concerns the temperature dependence of the maximum of the diffusion coefficient on a periodic lattice when there is an external force along a crystallographic axis. This temperature dependence, as well as an apparent scaling law associated with it, remain to be explained.

ACKNOWLEDGMENTS

This work was supported by the MCyT (Spain) under project BFM2003-07850, by the Engineering Research Program of the Office of Basic Energy Sciences at the U. S. Department of Energy under Grant No. DE-FG02-04ER46179, and by a grant from the University of California Institute for México and the United States (UC MEXUS) and the Consejo Nacional de Ciencia y Tecnología de México (CoNaCyT). A.H.R. acknowledges support from CONACyT-Mexico through Grant J-42647-F.

REFERENCES

1. H. Risken, 1989 *The Fokker–Planck Equation*, Springer Verlag, New York, 1989, Chapter 11.
2. J. M. Sancho, A. M. Lacasta, K. Lindenberg, I. M. Sokolov, and A. H. Romero, *Phys. Rev. Lett.* **92**, 250601 (2004).
3. A. M. Lacasta, J. M. Sancho, A. H. Romero, I. M. Sokolov, and K. Lindenberg, *Phys. Rev. E* **70**, 051104 (2004).
4. K. Lindenberg, A. M. Lacasta, J. M. Sancho, and A. H. Romero, *New J. Phys.* **7**, 29 (2005).
5. A. M. Lacasta, J. M. Sancho, A. H. Romero, and K. Lindenberg, *Phys. Rev. Lett.* **94**, 160601 (2005).
6. K. Lindenberg, A. M. Lacasta, J. M. Sancho, and A. H. Romero, *Proceedings of SPIE* **5845**, XXX (2005).
7. J. M. Sancho, A. M. Lacasta, K. Lindenberg, I. M. Sokolov, and A. H. Romero, *Phys. Rev. Lett.* **94**, 188902 (2005).
8. J-D. Bao and Y. Zhou, *Phys. Rev. Lett.* **94**, 188901 (2005).