Available online at www.sciencedirect.com
ScienceDirect
ELSEVIER
Physica A 375 (2007) 239–246
PHYSICA A
www.elsevier.com/locate/physa

Etched glass surfaces, atomic force microscopy and stochastic analysis

G.R. Jafari[a,b,*], M. Reza Rahimi Tabar[c,d], A. Iraji zad[c], G. Kavei[e]

[a]Department of Physics, Shahid Beheshti University, Evin, Tehran 19839, Iran
[b]Department of Nano-Science, IPM, P.O. Box 19395-5531, Tehran, Iran
[c]Department of Physics, Sharif University of Technology, P.O. Box 11365-9161, Tehran, Iran
[d]CNRS UMR 6529, Observatoire de la Côte d'Azur, BP 4229, 06304 Nice Cedex 4, France
[e]Material and Energy, Research Center, P.O. Box 14155-4777, Tehran, Iran

Received 4 December 2005; received in revised form 14 August 2006
Available online 10 October 2006

Abstract

The effect of etching time scale of glass surface on its statistical properties has been studied using atomic force microscopy technique. We have characterized the complexity of the height fluctuation of an etched surface by the stochastic parameters such as intermittency exponents, roughness, roughness exponents, drift and diffusion coefficients and found their widths in terms of the etching time.
© 2006 Elsevier B.V. All rights reserved.

Keywords: Etching process; Rough surface; Stochastic process

1. Introduction

The complexity of rough surfaces is the subject of a large variety of investigations in different fields of science [1,2]. Surface roughness has an enormous influence on many important physical phenomena such as contact mechanics, sealing, adhesion, friction and self-cleaning paints and glass windows [3,4]. A surface roughness of just a few nanometers is enough to remove the adhesion between clean and (elastically) hard solid surfaces [3]. The physical and chemical properties of surfaces and interfaces are to a significant degree determined by their topographic structure. The technology of micro-fabrication of glass is getting more and more important because glass substrates are currently being used to fabricate micro-electro-mechanical system (MEMS) devices [5]. Glass has many advantages as a material for MEMS applications, such as good mechanical and optical properties. It is a high electrical insulator, and it can be easily bonded to silicon substrates at temperatures lower than the temperature needed for fusion bonding [6]. Also micro- and nano-structuring of glass surfaces is important for the production of many components and systems such as

*Corresponding author. Department of Physics, Shahid Beheshti University, Evin, Tehran 19839, Iran.
E-mail address: gjafari@gmail.com (G.R. Jafari).

0378-4371/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.physa.2006.09.012

gratings, diffractive optical elements, planar wave guide devices, micro-fluidic channels and substrates for (bio) chemical applications [7]. Wet etching is also well developed for some of these applications [8–14].

One of the main problems in the rough surface is the scaling behavior of the moments of height h and evolution of the probability density function (PDF) of h, i.e. $P(h,x)$ in terms of the length scale x. Recently some authors have been able to obtain a Fokker–Planck equation describing the evolution of the probability distribution function in terms of the length scale, by analyzing some stochastic phenomena, such as rough surfaces [15–17], turbulent system [18], financial data [19], cosmic background radiation [20] and heart interbeats [21], etc. They noticed that the conditional probability density of field increment satisfies the Chapman–Kolmogorov equation. Mathematically, this is a necessary condition for the fluctuating data to be a Markovian process in the length (time) scales [22].

In this work, we investigate the etching process as a stochastic process. We measure the intermittency exponents of height structure function, roughness, roughness exponents and Kramers–Moyal's (KM) coefficients. Indeed we consider the etching time t, as an external parameter, to control the statistical properties of a rough surface and find their variations with t. It is shown that the first and second KM's coefficients have well-defined values, while the third and fourth order coefficients tend to zero. The first and second KM's coefficients for the fluctuations of $h(x)$ enable us to explain the height fluctuation of the etched glass surface.

2. Experimental

We started with glass microscope slides as a sample. Only one side of the sample was etched by HF solution for different etching times (less than 20 min). The HF concentration was 40% for all the experiments. The surface topography of the etched glass samples in the scale ($<5\,\mu$m) was obtained using an AFM (Park Scientific Instruments). The images in this scale were collected in a constant force mode and digitized into 256×256 pixels. A commercial standard pyramidal Si_3N_4 tip was used. A variety of scans, each with size L, were recorded at random locations on the surface. Fig. 1 shows typical AFM image with resolutions of about 20 nm.

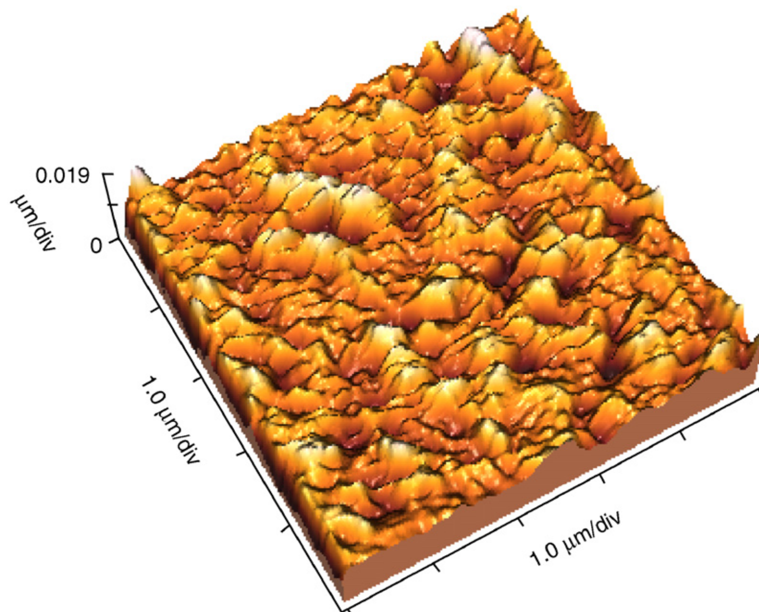

Fig. 1. AFM surface image of etched glass film with size $5 \times 5\,\mu m^2$ after 12 min.

3. Statistical quantities

3.1. Multifractal analysis and the intermittency exponent

Assuming statistical translational invariance, the structure functions $S^q(l) = \langle |h(x+l) - h(x)|^q \rangle$ (moments of the increment of the rough surface height fluctuation $h(x)$) will depend only on the space deference of heights l, and has a power law behavior if the process has the scaling property

$$S^q(l) = \langle |h(x+l) - h(x)|^q \rangle \propto S^q(L_0)\left(\frac{l}{L_0}\right)^{\xi(q)}, \tag{1}$$

where L_0 is the fixed largest length scale of the system, $\langle \cdots \rangle$ denotes statistical average (for non-overlapping increments of length l), q is the order of the moment (we take here $q>0$), and $\xi(q)$ is the exponents of structure function. The second moment is linked to the slope β of the Fourier power spectrum: $\beta = 1 + \xi_2$. The main property of a multifractal process is that it is characterized by a non-linear ξ_q function versus q. Monofractals are the generic result of this linear behavior. For instance, for Brownian motion (Bm) $\xi_q = q/2$, and for fractional Brownian motion (fBm) $\xi_q \propto q$.

3.2. Roughness and roughness exponents

It is also known that to derive the quantitative information of the surface morphology one may consider a sample of size L and define the mean height of growing film $\overline{h}$ and its *variance*, σ by

$$\sigma(L,t) = (\langle (h - \overline{h})^2 \rangle)^{1/2}, \tag{2}$$

where t is etching time and $\langle \cdots \rangle$ denotes an averaging over different samples, respectively. Moreover, etching time is a factor which can be applied to control the surface roughness of thin films.

Let us now also calculate the roughness exponent of the etched glass. Starting from a flat interface (one of the possible initial conditions), it is conjectured that a scaling of space by factor b and of time by factor b^z (z is the dynamical scaling exponent) rescales the variance σ by factor b^χ as follows [1]:

$$\sigma(bL, b^z t) = b^\alpha \sigma(L,t) \tag{3}$$

which implies that

$$\sigma(L,t) = L^\alpha f(t/L^z). \tag{4}$$

For large t and fixed L ($x = t/L^z \to \infty$) σ saturates. However, for fixed large L and $t \ll L^z$, one expects that correlations of the height fluctuations are set up only within a distance $t^{1/z}$ and thus must be independent of L. This implies that for $x \ll 1, f(x) \sim x^\beta$ with $\beta = \alpha/z$. Thus dynamic scaling postulates that

$$\sigma(L,t) \propto \begin{cases} t^\beta, & \mathrm{t} \ll L^z, \\ L^\alpha, & \mathrm{t} \gg L^z. \end{cases} \tag{5}$$

The roughness exponent α and the dynamic exponent β characterize the self-affine geometry of the surface and its dynamics, respectively.

The common procedure to measure the roughness exponent of a rough surface is the use of surface structure function depending on the length scale l which is defined as

$$S^2(l) = \langle |h(x+l) - h(x)|^2 \rangle. \tag{6}$$

It is equivalent to the statistics of height–height correlation function $C(l)$ for stationary surfaces, i.e. $S^2(l) = 2\sigma^2(1 - C(l))$. The second order structure function $S(l)$ scales with l as $l^{2\alpha}$ [1].

3.3. The Markov nature of height fluctuations: drift and diffusion coefficients

We check whether the data of height fluctuations follow a Markov chain and, if so, measure the Markov length scale l_M. As is well known, a given process with a degree of randomness or stochasticity may have a

finite or an infinite Markov length scale [23]. The Markov length scale is the minimum length interval over which the data can be considered as a Markov process. To determine the Markov length scale l_M, we note that a complete characterization of the statistical properties of random fluctuations of a quantity h in terms of a parameter x requires evaluation of the joint PDF, i.e. $P_N(h_1, x_1; \ldots; h_N, x_N)$, for any arbitrary N. If the process is a Markov process (a process without memory), an important simplification arises. For this type of process, P_N can be generated by a product of the conditional probabilities $P(h_{i+1}, x_{i+1}|h_i, x_i)$, for $i = 1, \ldots, N-1$. As a necessary condition for being a Markov process, the Chapman–Kolmogorov equation,

$$P(h_2, x_2|h_1, x_1) = \int \mathrm{d}(h_i) P(h_2, x_2|h_i, x_i) P(h_i, x_i|h_1, x_1), \tag{7}$$

should hold for any value of x_i, in the interval $x_2 < x_i < x_1$ [22].

The simplest way to determine l_M for homogeneous surface is the numerical calculation of the quantity, $S = |P(h_2, x_2|h_1, x_1) - \int \mathrm{d}h_3 P(h_2, x_2|h_3, x_3) P(h_3, x_3|h_1, x_1)|$, for given h_1 and h_2, in terms of, for example, $x_3 - x_1$ and considering the possible errors in estimating S. Then, $l_M = x_3 - x_1$ for that value of $x_3 - x_1$ such that, $S = 0$ [23].

It is well known, the Chapman–Kolmogorov equation yields an evolution equation for the change of the distribution function $P(h, x)$ across the scales x. The Chapman–Kolmogorov equation formulated in a differential form yields a master equation, which can take the form of a Fokker–Planck equation [22,23]:

$$\frac{\partial}{\partial x} P(h, x) = [-\frac{\partial}{\partial h} D^{(1)}(h, x) + \frac{\partial^2}{\partial h^2} D^{(2)}(h, x)] P(h, x). \tag{8}$$

The drift and diffusion coefficients $D^{(1)}(h, r)$, $D^{(2)}(h, r)$ can be estimated directly from the data and the moments $M^{(k)}$ of the conditional probability distributions:

$$D^{(k)}(h, x) = \frac{1}{k!} \lim_{r \to 0} M^{(k)},$$

$$M^{(k)} = \frac{1}{r} \int \mathrm{d}h' (h' - h)^k P(h', x + r|h, x). \tag{9}$$

The coefficients $D^{(k)}(h, x)$'s are known as Kramers–Moyal coefficients. According to Pawula's theorem [22], the Kramers–Moyal expansion stops after the second term, provided that the fourth order coefficient $D^{(4)}(h, x)$ vanishes [22]. The forth order coefficients $D^{(4)}$ in our analysis was found to be about $D^{(4)} \simeq 10^{-4} D^{(2)}$. In this approximation, we can ignore the coefficients $D^{(n)}$ for $n \geqslant 3$. We note that this Fokker–Planck equation is equivalent to the following Langevin equation (using the Ito interpretation) [22]:

$$\frac{\partial}{\partial x} h(x) = D^{(1)}(h, x) + \sqrt{D^{(2)}(h, x)} f(x), \tag{10}$$

where $f(x)$ is a random force, zero mean with Gaussian statistics, δ-correlated in x, i.e. $\langle f(x) f(x') \rangle = 2\delta(x - x')$. Furthermore, with this last expression, it becomes clear that we are able to separate the deterministic and the noisy components of the surface height fluctuations in terms of the coefficients $D^{(1)}$ and $D^{(2)}$.

4. Results and discussion

Now, using the introduced statistical parameters in the previous sections, it is possible to obtain some quantitative information about the effect of etching time on surface topography of the glass surface. To study the effect of the etching time on the surface statistical characteristics, we have utilized an AFM imaging technique in order to obtain micro-structural data of the etched glass surfaces at the different etching times in the HF. Fig. 1 shows the AFM image of etched glass after 12 min of etching. To investigate the scaling behavior of the moments of $\delta h_l = h(x + l) - h(x)$, we consider the samples that reached the stationary state. This means that their statistical properties do not change with time. In our case the samples with an etching time of more than 20 min are almost stationary. Fig. 2 shows the log–log plot of the structure functions versus length scale l for different orders of moments. The straight lines show that the moments of order q have the

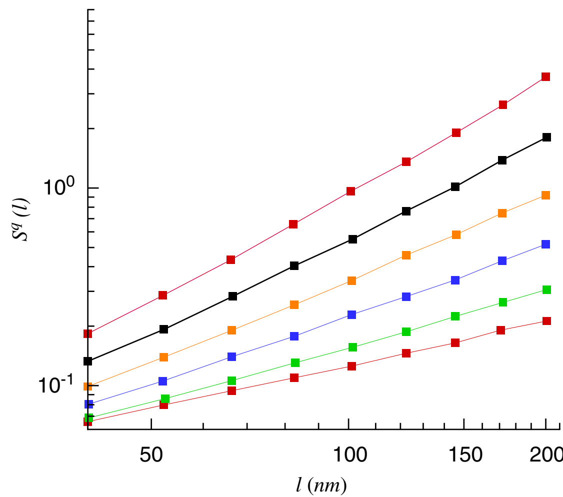

Fig. 2. Scaling of the structure functions in log–log plot for moments less than 8. (from bottom to top).

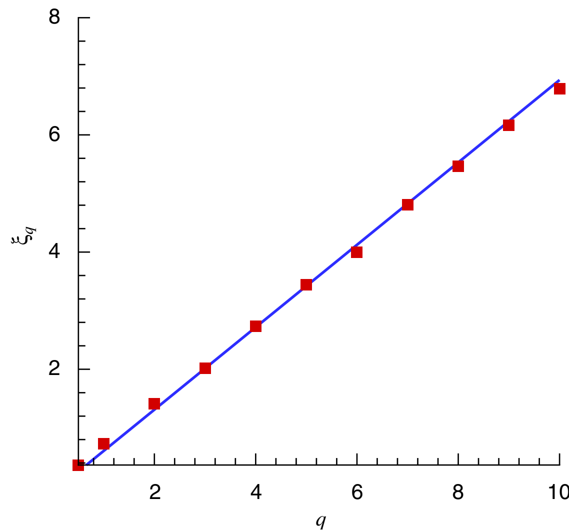

Fig. 3. The results of scaling exponent ξ_q which is clearly linear vs. q.

scaling behavior. We have checked the scaling relation up to moment $q = 10$. The resulting intermittency exponent ξ_q is shown in Fig. 3. It is evident that ξ_q has a linear behavior. This means that the height fluctuations are mono-fractal behavior. We also directly estimated the scaling exponent of the linear term $l^{qH}/\langle(h(x+l)-h(x))^q\rangle$ and obtained the following values for the samples with 20 min etching time, $\xi_1 = 0.70 \pm 0.04$ and $\xi_2 = 1.40 \pm 0.04$. This means etching memorizes fractal features during etching. Therefore using the scaling exponent ξ_2 we obtain the roughness exponent α as $\xi_2/2 = 0.70 \pm 0.04$. Fig. 4 presents the structure function $S(l)$ of the surface at the different etching times, using Eq. (6). It is also possible to evaluate the grain size dependence on the etching time, using the correlation length achieved by the structure function represented in Fig. 4. The correlation lengths increase with etching time. Its value has an exponential behavior $448(1-\exp(-0.15t))$ nm. Also we find that the dynamical exponent is given by $\beta = 0.6 \pm 0.1$. Also we measured the variation of the Markov length with etching time t (min), and obtain $l_M = 40 + 3t$ (nm) for time scales $t < 20$ min.

Finally, to obtain the stochastic equation of the height fluctuation behaviors of the surface, we need to measure the Kramer–Moyal Coefficients. In our analysis the forth order coefficients $D^{(4)}$ is less than second

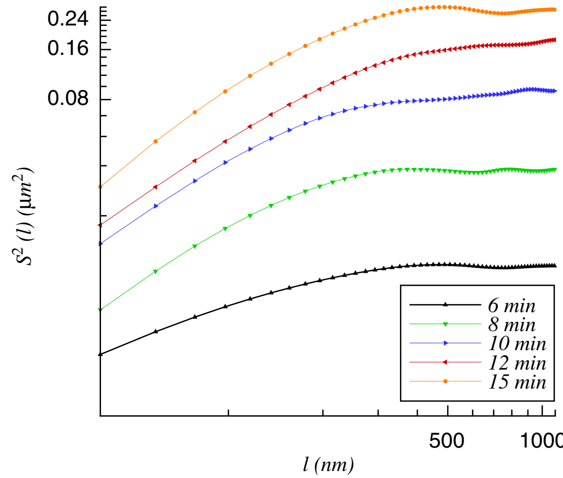

Fig. 4. Log–Log plot of selection structure function of the etched glass surfaces.

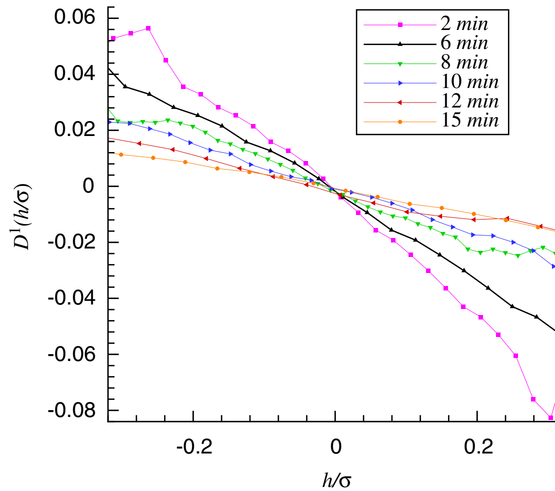

Fig. 5. Drift coefficients of the surfaces at different etching times less than 20 min.

order coefficients, $D^{(2)}$, about $D^{(4)} \simeq 10^{-4} D^{(2)}$. In this approximation, according to Pawula's theorem [22], we ignored the coefficients $D^{(n)}$ for $n \geqslant 3$. Therefore to discuss the surfaces, we need just measure the drift coefficient $D^{(1)}(h/\sigma)$ and diffusion coefficient $D^{(2)}(h/\sigma$ using Eq. (9). Figs. 5 and 6 show the drift coefficient $D^{(1)}(h/\sigma)$ and diffusion coefficients $D^{(2)}(h/\sigma)$ for the surfaces at the different etching times, respectively. It can be shown that the drift and diffusion coefficients have the following behavior:

$$D^{(1)}\left(\frac{h}{\sigma}, t\right) = -f^{(1)}(t)\frac{h}{\sigma}, \tag{11}$$

$$D^{(2)}\left(\frac{h}{\sigma}, t\right) = f^{(2)}(t)\left(\frac{h}{\sigma}\right)^2. \tag{12}$$

The two coefficients $f^{(1)}(t)$ and $f^{(2)}(t)$ increase with the h/σ and is then saturated. Using the data analysis we obtain that they are linear versus time (min): $f^{(1)}(t) = 0.005t$ and $f^{(2)}(t) = 0.0003t$ for time scales $t < 20$ min. To better compare the parameters of samples we divided the heights to their variances. In this case, maximum and minimum of heights are about plus 1 and minus 1, respectively. Comparing samples with etching times 2 and

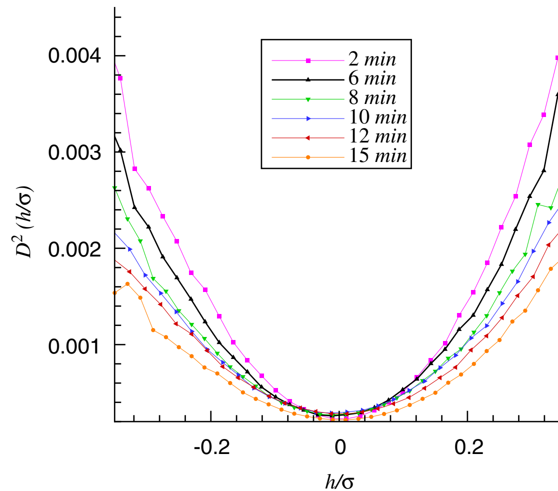

Fig. 6. Diffused coefficients of the surface at different etching times less than 20 min.

6 min shows $f^{(1)}$ increases 300% after 4 min (from 2 to 6 min) from $f^{(1)}(t = 2 \times 60) = 0.6$ to $f^{(1)}(t = 6 \times 60) = 1.8$. Also, $f^{(2)}$ is 0.006 and 0.018 after 2 and 6 min, respectively.

5. Conclusion

We have investigated the role of etching time, as an external parameter, to control the statistical properties of a rough surface. We have shown that in the saturated state the structure of topography has fractal features with fractal dimension $D_f = 1.30$. In addition, Langevin characterization of the etched surfaces enables us to regenerate the rough surfaces grown at the different etching times, with the same statistical properties in the considered scales [15].

Acknowledgments

We would like to thank S.M. Mahdavi for his useful comments and discussions and also P. Kaghazchi and M. Shirazi for sample preparation.

References

[1] A.L. Barabasi, H.E. Stanley, Fractal Concepts in Surface Growth, Cambridge University Press, New York, 1995.
[2] S. Davies, P. Hall, J. Roy. Stat. Soc. B 61 (1999) 3.
[3] A.G. Peressadko, N. Hosoda, B.N.J. Persson, PRL 95 (2005) 124301;
B.N.J. Persson, O. Albohr, U. Tartaglino, A.I. Volokitin, E. Tosatti, J. Phys. Condens. Matter 17 (2005) R1–R62.
[4] Y.-P. Zhao, L.S. Wang, T.X. Yu, J. Adhes. Sci. Technol. 17 (2003) 519.
[5] W.I. Jang, C.A. Choi, M.L. Lee, C.H. Jun, Y.T. Kim, J. Micromech. Microeng. 12 (2002) 297306.
[6] M. Bu, T. Melvina, G.J. Ensell, J.S. Wilkinson, A.G.R. Evans, Sensors and Actuators A 115 (2004) 476–482.
[7] Y.-C. Lin, H.-C. Ho, C.-K. Tseng, S.-Q. Hou, J. Micromech. Microeng. 11 (2001) 189–194.
[8] D.M. Knotter, J. Am. Chem. Soc. 122 (2000) 4345.
[9] G.A.C.M. Spierings, J. Mater. Sci. 28 (1993) 6261.
[10] R. Schuitema, et al., Light scattering at rough interfaces of thin film solar cells to improve the efficiency and stability, IEEE/ProRISC99, 1999, pp. 399–404.
[11] L.B. Glebov, et al., Photo induced chemical etching of silicate and borosilicate glasses, Glasstech. Ber. Glass Sci. Technol. 75 (C2) (2002) 298–301.
[12] G.R. Jafari, S.M. Mahdavi, A. Iraji zad, P. Kaghazchi, Surf. Interface Anal. 37 (2005) 641–645.
[13] N. Silikas, k.E.R. England, D. C Wattes, K. D Jandt, J. Dent. 27 (1999) 137.
[14] A. Irajizad, G. Kavei, M.R.R. Tabar, S.M.V. Allaei, J. Phys. Condens. Matter 15 (2003) 1889.
[15] G.R. Jafari, S.M. Fazeli, F. Ghasemi, S.M.V. Allaei, M.R.R. Tabar, A. Irajizad, G. Kavei, Phys. Rev. Lett. 91 (2003) 226101.

[16] M. Waechter, F. Riess, Th. Schimmel, U. Wendt, J. Peinke, Eur. Phys. J. B 41 (2004) 259–277.
[17] P. Sangpour, G.R. Jafari, O. Akhavan, A.Z. Moshfegh, M.R.R. Tabar, Phys. Rev. B 71 (2005) 155423.
[18] C. Renner, J. Peinke, R. Friedrich, J. Fluid Mech. 433 (2001) 383409.
[19] Ch. Renner, J. Peinke, R. Friedrich, Physica A 298 (2001) 499.
[20] F. Ghasemi, A. Bahraminasab, S. Rahvar, M. Reza Rahimi Tabar, preprint arxiv:astro-phy/0312227, 2003.
[21] F. Ghasemi, J. Peinke, M. Sahimi, M. Reza Rahimi Tabar, Eur. Phys. J. B 47 (2005) 411.
[22] H. Risken, The Fokker–Planck Equation, Springer, Berlin, 1984.
[23] R. Friedrich, J. Zeller, J. Peinke, Europhys. Lett. 41 (1998) 153.