PHYSICAL REVIEW E **84**, 050602(R) (2011)

# Persistence in reactive-wetting interfaces

Yael Efraim* and Haim Taitelbaum
*Department of Physics, Bar-Ilan University, Ramat-Gan 52900, Israel*
(Received 26 April 2011; published 28 November 2011)

In this paper, we report on persistence results of reactive-wetting advancing interfaces performed with mercury on silver at room temperature. Earlier kinetic roughening studies of reactive-wetting systems at room temperature as well as at high temperatures revealed some limited information on the spatiotemporal behavior of these systems. However, by calculating the persistence exponent, we were able to identify two distinct kinetic time regimes in this process. In the first one, while the interface is moving but its width is not yet growing, the persistence exponent is $\theta = 0.55 \pm 0.05$, which is typical for a random, noisy behavior. In the second regime, there is an effective growth of the interface width with a growth exponent $\beta = 0.67 \pm 0.06$ followed by saturation, according to the Family-Vicsek description of interface growth. The persistence exponent in this regime is $\theta = 0.37 \pm 0.05$, which indicates that the relation $\theta = 1 - \beta$ seems to hold even for this nonlinear experimental system.

DOI: 10.1103/PhysRevE.84.050602 PACS number(s): 68.08.Bc, 05.40.−a, 89.75.Da, 02.50.−r

Many problems in physics require an understanding of the stochastic dynamics of spatially extended objects. Traditionally, the spatial and dynamical properties of such systems are described in terms of space- and time-dependent correlation functions and scaling exponents [1]. In recent years, there has been significant interest in studies of the first-passage properties of dynamical fluctuations [2], quantified in terms of *persistence probability*. The persistence probability $P(t)$ is the probability that a stochastic variable will never cross some reference level within time interval $t$. The persistence probability was calculated and measured for several theoretical, numerical, and experimental systems [3–7] and was shown to decrease with time as a power law,

$$P(t) \sim t^{-\theta}, \tag{1}$$

where $\theta$ is the *persistence exponent*. The persistence exponent $\theta$ is a nontrivial exponent that depends on the history of the system and is sensitive to hidden temporal correlations. This high sensitivity is particularly useful in systems in which the assignment of a universality class is ambiguous [8].

The highly widespread process of wetting, e.g., the spreading of a liquid droplet on solid substrates, is important in many fields and has been studied extensively. One of the more interesting cases is reactive wetting [9–11], where the materials involved in the wetting process also react chemically. The reaction changes dramatically the characteristics of the process and induces different kinetic behavior as well as nonlinear effects [12]. Our reactive-wetting *room-temperature* experimental system is a small Hg droplet spreading on a thin Ag substrate. The geometry and dynamics of the interface between the two metals, i.e., the triple line, are the focus of this study. A typical optical microscope top-view snapshot of a small part of the interface is shown in Fig. 1.

The kinetic roughening properties of an interface of length $L_0$ are defined on the basis of its width $W(L,t)$, which is simply the second moment of the interface height $h(x,t)$ (see Fig. 1),

$$W(L,t) = \sqrt{\langle h^2(x,t)\rangle - \langle h(x,t)\rangle^2}, \tag{2}$$

where the angular brackets denote spatial averaging over interface segments of length $L$. According to the Family-Vicsek relation [1],

$$W(L,t) \sim \begin{cases} t^{\beta}, & t \ll t^*, \\ L^{\alpha}, & t \gg t^*, \end{cases} \tag{3}$$

where $t^*$ is given in terms of the system size $L_0$ as

$$t^* \sim L_0^{\alpha/\beta}. \tag{4}$$

The *growth exponent* $\beta$ describes the dynamics of the interface, while the *roughness exponent* $\alpha$, which is measured after the interface width reaches saturation, describes the morphology at the final stages. Naturally, a relation between the two temporal measures, the growth exponent $\beta$ and the persistence exponent $\theta$, is expected. Indeed, it was shown [5] that in linear systems,

$$\theta = 1 - \beta. \tag{5}$$

This implies, e.g., that the persistence exponent of a random walk, whose growth exponent is known to be $\beta = 1/2$, is $\theta = 1/2$ [5]. Relation (5) was proved for linear systems only; however, it was found to be valid not only in linear experimental systems [13] but also in some nonlinear experimental systems [7], Therefore this relation might be more general.

For the nonlinear Kardar-Parisi-Zhang (KPZ) equation [14], the persistence exponent value depends on the direction in which the reference level is crossed, i.e., $\theta_{\pm}$ is the persistence exponent of the probability not to cross the reference level from bottom up (+) and from top down (−), respectively [12]. This difference, originating from the up-down symmetry breaking in nonlinear systems [1], was not supported by experimental results [7,15].

In this work, we study the persistence probability in the above-mentioned reactive-wetting experiment at room temperature. This study utilizes the persistence concept for this complex, yet partially understood, reactive-wetting interface phenomenon. We show that implying the new persistence statistical tool contributes valuable information into this complex process.

The reactive-wetting process of a 150 $\mu$m Hg droplet spreading on a 4000-Å-thick Ag substrate is observed using an optical microscope (Zeiss) and is recorded by a charge-coupled

*yaelhos@gmail.com

 

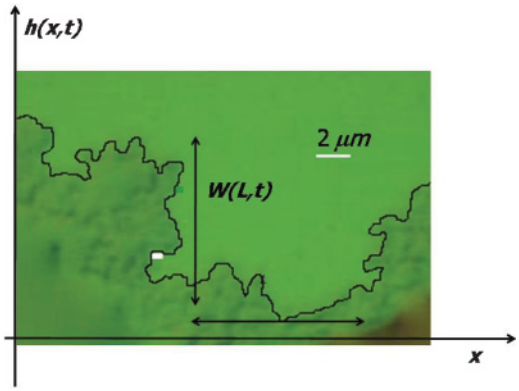


FIG. 1. (Color online) Typical top-view snapshot of the Hg-Ag interface at a given time. The height of the interface is $h(x,t)$ and its second moment is defined as the interface width $W(L,t)$ [see Eq. (2)].

device (CCD) camera that is mounted on top of the microscope (a detailed description of the experimental setup is available in [9,10,16–19]). The real-time recording of the reactive-wetting evolution from the top view is cut into a series of snapshots with a time interval of 0.5 s between successive frames. This time interval was chosen as it is much larger than the time scale of reaction (less than a millisecond) and much smaller than the time scale of the entire process (several minutes). The interface shape and position are extracted from each frame, so that one has a series of $h(x,t)$ data describing the interface shape at each time (see Fig. 1). From these numerical data, we compute $W(L,t)$ for each window size from 1 pixel ($\sim$0.083 $\mu$m) to $L_0/2$ ($\sim$12.5 $\mu$m), and for each time.

We define the persistence measure in our experimental system as follows: We first define the stochastic variable in the system as the net height $h^*$ of a given point $x$ on the interface with respect to the spatial average of the interface height $\langle h(x,t)\rangle$ at each time, $h^*(x,t) = h(x,t) - \langle h(x,t)\rangle$. This definition of the net height eliminates the overall motion of the contact line. We then plot the net height trajectory of this single point as a function of time and divide the time axis into intervals of different lengths [Fig. 2(a)]. The reference level, up to which a point will be considered "persistent," is the location of the point *at the beginning of each time interval* $h^*(x,t_0)$. For each interval length $t$, we calculate the probability $P(x,t_0,t_0+t)$ [6],

$$P(x,t_0,t_0+t) = \Pr\{\mathrm{sgn}[h^*(x,t_0+t') - h^*(x,t_0)] \text{ remains the same for all } 0 < t' < t\}. \quad (6)$$

We next average over all possible $t_0$ and all points $x$ on the interface in order to get the persistence probability,

$$\langle\langle P(x,t_0,t_0+t)\rangle_{t_0}\rangle_x \to P(t). \quad (7)$$

A closely related first-passage measure is the *survival probability* $S(t)$ [6]. The survival probability is similar to the persistence, except from the reference level, which is *fixed* for all intervals at the origin, $h^* = 0$ [Fig. 2(b)]. Hence the probability for a point to "survive" is

$$S(x,t_0,t_0+t) = \Pr\{\mathrm{sgn}[h(x,t_0+t')] \text{ remains the same for all } 0 < t' < t\}, \quad (8)$$

and then $\langle\langle S(x,t_0,t_0+t)\rangle_{t_0}\rangle_x \to S(t)$.

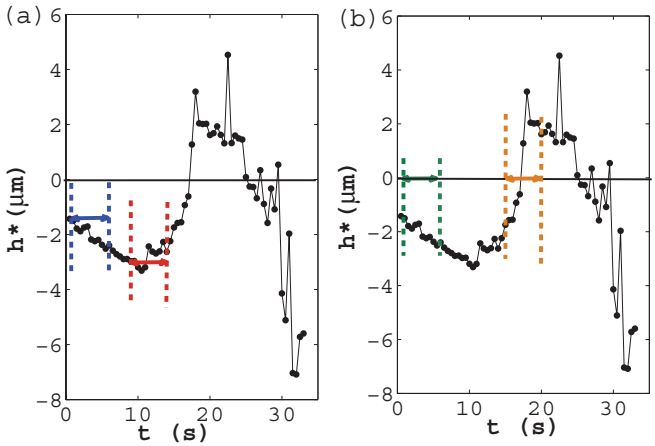


FIG. 2. (Color online) Trajectory of a single interface point. (a) *Persistence*. Two intervals of length $t = 5$ s are marked. Each reference level is defined by $h^*$ at its starting point $t_0$. The interval starting at $t_0 = 1$ s (blue) is "persistent" but the one starting at $t_0 = 9$ s (red) is not. (b) *Survival*. The reference level is fixed at the origin, $h^* = 0$. Two intervals of length $t = 5$ s are marked. The one starting at $t_0 = 1$ s (green) is "surviving" but the one starting at $t_0 = 15$ s (orange) is not.

This seemingly minor change in the definition generates large difference in the probability distribution. While the persistence probability decays as a *power law* [Eq. (1)], the survival probability decays *exponentially*, with a survival time scale $\tau_s$ [13],

$$S(t) \propto e^{-t/\tau_s}. \quad (9)$$

More than a dozen independent experiments were analyzed in this study. For each single experiment, we calculated the persistence and survival probabilities as well as the growth and roughness exponents.

According to Eq. (3), the interface width $W$ as a function of time in a log-log scale should yield a straight line with a slope $\beta$ followed by saturation to the regime where $\alpha$ can be calculated. In Fig. 3(a), we show $W(t)$ for a typical *single* experiment. This plot resembles the one predicted by Eq. (3), but there is also a preliminary regime where $W(t)$ is approximately constant. In this regime, the interface develops, its shape is changing, but its overall width is (nonzero) constant. This calls for a sensitive microscopic tool, such as the persistence probability, which can reflect the fine progression of the interface in this regime. Furthermore, the nonlinear experimental system provides an opportunity to examine whether Eq. (5) is restricted only to linear systems or whether it can be valid also in nonlinear processes such as reactive-wetting interfaces. Therefore, we find it adequate to imply the persistence concept for this complex system.

We first calculate the persistence probability of each experiment. Surprisingly, we find that in most experiments the probability function is not just the known power-law decay. As shown in Fig. 3(b), the persistence probability decays as a power law, with an average persistence exponent of $\theta = 0.55 \pm 0.05$ along the preliminary time regime. However, at the border between the preliminary to the growth regime, it "breaks" to a much larger negative slope. This behavior

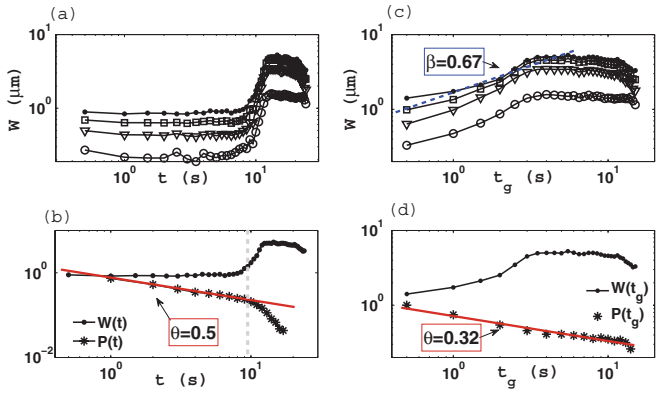


FIG. 3. (Color online) (a) $W(t)$ (log-log scale) of a *single* reactive-wetting experiment, for different segment sizes $L$ (from bottom up: 2.5, 6, 9, and 12.5 $\mu$m). (b) $W(t)$ and $P(t)$ (log-log scale) for a *single* experiment (and for $L = 12.5$ $\mu$m). At the initial regime, the persistence exponent is $\theta = 0.5$, then $P(t)$ breaks into a much larger slope. (c) Same data as in (a) but the time axis is shifted so that $t_g = 0$ is where the growth regime starts. The slope is the growth exponent $\beta$. (d) $W(t_g)$ and $P(t_g)$ (log-log scale) for the Family-Vicsek regime. The persistence exponent is $\theta = 0.32$ during both growth and saturation regimes.

was reproducible in most experiments and was found to be an accurate indicator of the border between the two regimes, which is often unclear due to the noisy nature of $W(t)$ and to the variation between different sets of experiments. Moreover, the value of the persistence exponent in the first regime hints at the random-noisy nature of the reactive-wetting process in its early stages, since the persistence exponent of $\theta \approx 0.5$ corresponds to a random walk [5]. We next address the known Family-Vicsek relation by shifting the time axis so that $t_g = 0$ is where the persistence probability loses its initial slope [Fig. 3(c)]. The persistence measure is sensitive to the initial conditions and to the entire history of the process, hence after cutting the first regime out, one needs to repeat the calculation for the growth regime only.

In Fig. 3(d), we show the results for a single experiment in which $\theta \approx 0.32$. An average over all experiments yields a persistence exponent in the growth regime, $\theta = 0.37 \pm 0.05$. In this calculation, the power-law trend of the persistence probability extends into the saturation regime. This indicates an essential difference between the initial and saturation regimes. In both regimes, the width is a nonzero constant; however, while the saturation is a part of the entire growth process, a different mechanism is generating the system in the initial regime. It changes when the growth starts, and results in a "break" in the persistence probability function.

The overall growth of the interface width is accompanied by a persistence exponent that is smaller than that in the early regime, meaning that the system is more persistent. It is indeed reasonable that points along the interface are more "persistent" during growth, i.e., points that are moving forward keep advancing and points that are far behind keep dawdling, causing the effective width to grow. Averaging over all the experiments, the growth exponent $\beta$ in this regime is found to be $\beta = 0.67 \pm 0.06$. This value is in agreement with former experiments in a similar system and with simulation results of the quenched Kardar-Parisi-Zhang (QKPZ) equation [17,20–22]. This also means that relation (5) is valid in the growth regime, $\theta + \beta = 1.04 \pm 0.07$. This is unexpected since the reactive-wetting experiment is known to be nonlinear; however, in the nonlinear experiment of the slow combustion of paper [7], the persistence and growth exponents of the combustion front were also found to obey relation (5). We also calculated separately the persistence probability so as not to cross the reference level from bottom up, $P_+$, and from top down, $P_-$. Although we found that usually $P_+ > P_-$, due to the overall drift of the interface upward, no significant difference in the persistence exponent values was found, i.e., in this system $\theta_+ \approx \theta_- \approx \theta$. This result is also in agreement with the nonlinear experimental system of the slow combustion of paper fronts [7].

For the survival probability in our reactive-wetting system, we found that the survival time $\tau_s$ depends strongly on the total measurement time $T$, therefore we calculated the ratio $\tau_s/T$, i.e., the *relative* survival time. In the preliminary regime, the survival time is about 35% of the entire measurement time, $\tau_s/T = 0.35 \pm 0.03$, while in the Family-Viscek regime it is much larger, $\tau_s/T_g = 0.63 \pm 0.03$, where $T_g$ is the total duration of the Family-Viscek regime. Again, it is reasonable that a longer survival time characterizes growth because it describes the trend of points along the interface staying far from the average for longer times. A detailed discussion about the survival probability in this experiment is available in [15].

To summarize, in the first preliminary regime, the persistence exponent indicates that the main mechanism that drives the interface is simply noise, which generates small random fluctuations in the initially smooth interface. In the growth regime, relation (5) is unexpectedly fulfilled, strengthening the conjecture that it is more general than theoretically predicted and is probably valid in nonlinear systems as well.

These different stages in the kinetic roughening of the reactive-wetting process resemble the microscopic description of interface development represented by the various terms in a family of nonlinear continuum equations [23]. A typical example is the KPZ equation [14]. In this equation,

$$\frac{\partial h(x,t)}{\partial t} = \upsilon \nabla^2 h(x,t) + \frac{\lambda}{2}(\nabla h)^2 + \eta(x,t), \qquad (10)$$

where stochastic noise $\eta$ generates small spatial gradient $\nabla h$ on the initially flat interface. This gradient grows nonlinearly $(\nabla h)^2$ and eventually competes with the relaxation term $\nabla^2 h$. These three terms determine the interface dynamics. We use the rational of this model in order to explain the macroscopic stages of the reactive-wetting experiment. In the first regime, the main mechanism is noise, which is not dominant enough to immediately cause overall growth, but its effect on the interface is accumulative. At some point, the accumulative noise leads to the overall growth of the interface width. This growth has to compete with relaxing mechanisms such as diffusion and surface tension; hence, there are usually fluctuations around the growth trend in this regime [20,21]. Finally, the process reaches quasiequilibrium and the interface width saturates. However, this is far from achieving true equilibrium because fine-structure changes still take place. The persistence concept allows one to better understand and clearly define these regimes.

The definitions of the different stages in the reactive-wetting process and their meaning, as revealed by the persistence measure, are complementary to recent findings about the reactive-wetting process (at *high* temperatures) from a chemical point of view [24]. This work defines four sequential stages of reactive-wetting in metal-metal systems. First, there is a very early and rather short (less than a second) time regime, in which the liquid spreads with no discernable morphological or chemical change of the interface. The very early regime is undetectable in our reactive-wetting experiment described above. The second regime, referred to in [24] as the *reactive-wetting regime*, is where reaction exerts a first-order effect on the spreading, and significant chemical changes of the interface can occur. Even though this regime is chemically dramatic, the interface shape in this stage is still not developing. Therefore, this regime, which is an essential part of the reactive-wetting process, cannot be described in the framework of standard kinetic roughening, i.e., the Family-Vicsek relation [Eq. (3)]. Indeed, according to our persistence study, the geometrical changes of the interface are random at this stage. The third regime is referred to in [24] as *the kinetic roughening regime*. In this regime, the interface width grows according to the Family-Vicsek relation [Eq. (3)]. This phenomenon was observed in several metal-metal reactive-wetting systems [11,18]. The fourth and final regime is when the interface stops advancing, its shape is more or less fixed, and for all practical purposes the experiment is over. The early stage of this regime is what we call here saturation. However, this regime is not a true equilibrium from both chemical and morphological points of view because minor changes of the interface structure still occur together with the slow chemical equilibration by diffusion [25].

In summary, the first-passage properties of the advancing interface, particularly the persistence probability, are an important tool for a better understanding of complex reactive-wetting processes. The persistence exponent value in the different regimes is a credible measure to identify the border between the regimes and to better recognize the main mechanism in each stage. In addition, this study gives further evidence for a nonlinear experimental system that obeys relation (5), supporting the conjecture that this relation is general.

We thank A. Be'er for his help during various stages of this project, and C. Dasgupta, J. Krug, and T.J. Singler for useful discussions.

[1] A. L. Barabasi and H. E. Stanley, *Fractal Concepts in Surface Growth* (Cambridge University Press, Cambridge, 1995).
[2] S. N. Majumdar, Curr. Sci. **77**, 370 (1999).
[3] B. Derrida, A. J. Bray, and C. Godreche, J. Phys. A **27**, L357 (1994).
[4] B. Derrida, V. Hakim, and V. Pasquier, Phys. Rev. Lett. **75**, 751 (1995).
[5] J. Krug, H. Kallabis, S. N. Majumdar, S. J. Cornell, A. J. Bray, and C. Sire, Phys. Rev. E **56**, 2702 (1997).
[6] M. Constantin, C. Dasgupta, S. Das Sarma, D. B. Dougherty, and E. D. Williams, J. Stat. Mech. (2007) P07011, and references cited therein.
[7] J. Merikoski, J. Maunuksela, M. Myllys, J. Timonen, and M. J. Alava, Phys. Rev. Lett. **90**, 024501 (2003).
[8] J. Krug, Physica A **340**, 647 (2004).
[9] A. Be'er, Y. Lereah, A. Frydman, and H. Taitelbaum, Phys. Rev. E **75**, 051601 (2007).
[10] A. Be'er, Y. Lereah, and H. Taitelbaum, Mater. Sci. Eng. A **495**, 102 (2008).
[11] L. Yin, A. Chauhan, and T. J. Singler, Mater. Sci. Eng. A **495**, 80 (2008).
[12] H. Kallabis and J. Krug, Europhys. Lett. **45**, 20 (1999).
[13] D. B. Dougherty, I. Lyubinetsky, E. D. Williams, M. Constantin, C. Dasgupta, and S. Das Sarma, Phys. Rev. Lett. **89**, 136102 (2002).
[14] M. Kardar, G. Parisi, and Y. -C. Zhang, Phys. Rev. Lett. **56**, 889 (1986).
[15] Y. Efraim, M. Sc. thesis, Bar Ilan University, Israel, 2008.
[16] A. Be'er, Y. Lereah, and H. Taitelbaum, Physica A **285**, 156 (2000).
[17] A. Be'er, Y. Lereah, I. Hecht, and H. Taitelbaum, Physica A **302**, 297 (2001).
[18] A. Be'er, Y. Lereah, A. Frydman, and H. Taitelbaum, Physica A **314**, 325 (2002).
[19] A. Be'er and Y. Lereah, J. Microsc. **208**, 148 (2002).
[20] A. Be'er, I. Hecht, and H. Taitelbaum, Phys. Rev. E **72**, 031606 (2005).
[21] I. Hecht, A. Be'er, and H. Taitelbaum, Fluct. Noise Lett. **5**, L319 (2005).
[22] Y. Efraim and H. Taitelbaum, Cent. Eur. J. Phys. **7**, 503 (2009).
[23] T. Halpin-Healy and Y. -C. Zhang, Phys. Rep. **254**, 215 (1995).
[24] L. Yin, B. T. Murray, S. Su, Y. Sun, Y. Efraim, H. Taitelbaum, and T. J. Singler, J. Phys. Condens. Matter **21**, 464130 (2009).
[25] L. Yin, B. T. Murray, and T. J. Singler, Act. Mater. **54**, 3561 (2006).