# The dynamics and geometry
# of solid–liquid reaction interface

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## Abstract

The spreading of small droplets (50–200 μm) of Hg on thin Ag films has been studied. The Hg front formation mechanism has been determined using optical microscope, Scanning Electron Microscope (SEM) and Atomic Force Microscope (AFM) analyses. The dynamics and geometry of the growing rough surfaces observed in our experiment, have been analyzed using the concepts of dynamic scaling and self-affine fractal geometry, in order to determine the corresponding roughness ($\alpha$) and growth ($\beta$) exponents. We have studied two systems, one in which the silver thickness was 500–2000 Å and the other where the silver thickness was 0.1 mm. We have found that $\alpha = 0.66 \pm 0.03$ and $\beta = 0.46 \pm 0.02$ in the first system, and $\alpha = 0.77 \pm 0.04$ and $\beta = 0.6 \pm 0.02$ in the second one. Each of these pairs satisfies the scaling law $\alpha + \alpha/\beta = 2$ within the experimental error. In addition, it was found, in both systems, that for final stages of the experiment, the roughness exponent $\alpha$ crosses over to $\alpha \approx 0.5$ for relatively long length scales (order of a few microns). These findings indicate that different mechanisms govern the process in various time and length regimes: diffusion and wetting at early stages, and chemical reaction at final stages and short-length scales. © 2000 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Spreading of liquids on solids and wetting of solid surfaces are rich physical, chemical, and statistical phenomena [1]. Modern statistical methods [2–5] of analyzing the interface between the liquid and the solid make use of two exponents to characterize
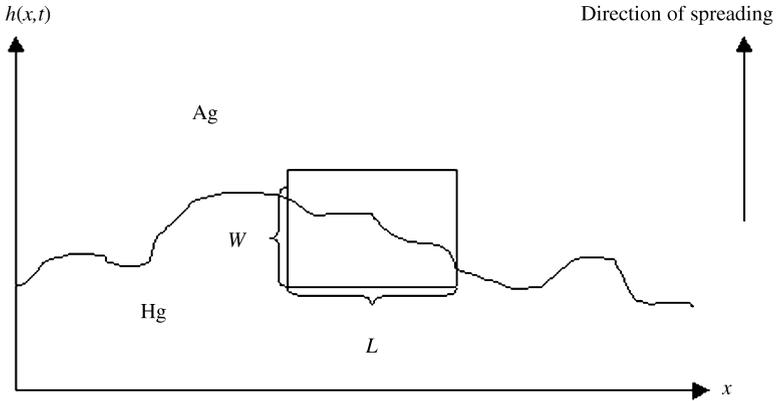
Fig. 1. A top view of a typical solid-liquid interface at a certain time in the spreading experiment. The width $W$ for every length $L$ is defined by Eq. (1).

the interface and associate it with a specific universality class. Generally, one can describe the interface by a function $h(x,t)$ (Fig. 1). A width function $W$ is defined as

$$W^2(L,t) = \langle h(x,t)^2 \rangle - \langle h(x,t) \rangle^2 , \tag{1}$$

where $L$ varies from the smallest length scale (say a single lattice unit) to the system size $L_0$. The width $W$ of the interface is related to the time $t$ and to $L$ by two scaling exponents, $\alpha$ and $\beta$ [5]

$$W \sim \begin{cases} t^\beta & t \ll t_0 , \\ L^\alpha & t \gg t_0 , \end{cases} \tag{2}$$

where $t_0 \approx L^{\alpha/\beta}$.

In most cases, the exponents indicate the mechanisms that govern the interface's growth (such as diffusion, surface tension, wetting, chemical reaction, etc.). Thus one can explore the universal system characteristics and apply it to a wide spectrum of scientific areas, including biology [6] and medicaments [7].

Specifically, we have studied the dynamics and geometry of the interface between liquid metal (Hg) and a thin metal (Ag) film. This experiment has three special aspects:

(i) It involves *chemical reactions* between the solid and the liquid in addition to other mechanisms such as diffusion, surface tension, wetting, etc. Such reaction creates inter-metallic compounds $Ag_3Hg_4$ and $Ag_4Hg_3$ [8] that may influence the structure of the interface and yield different exponents.

(ii) The film is very thin (500–2000 Å), thus the droplet can touch the glass and one can study possible *de-wetting* effects.

(iii) The experiment was recorded and analyzed *in situ* and not only at the end.

## 2. The experiment

### 2.1. Materials

We have studied two different systems. In the first system, Ag metallic films in various thicknesses (500–2000 Å) were deposited on microscope slides by vacuum evaporation. In the second system, a 0.1 mm foil of silver was polished by diamond powder in order to create a smooth surface. Small drops of Hg in various diameters (50–200 μm) were placed on these clean metal films' surfaces.

### 2.2. Set up and procedures

Spreading of Hg on the Ag surface has been observed using an optical microscope equipped with differential interference contrast (DIC). The Hg front propagation has been recorded by a video camera, which followed the spreading Hg front. The images were analyzed in order to determine their dynamic and geometrical properties. A few days after the experiment, the specimen has been examined by a Scanning Electron Microscope (SEM) and by an Atomic Force Microscope (AFM) in order to closely look at the geometrical and chemical structure of the interface.

## 3. Results and discussion

In general, we have realized that one should take into account the time passed from the preparation of the thin silver films until the actual spreading experiment. This is because the top layer of the silver is contaminated by different molecules, and its chemical and physical properties, such as surface tension coefficient, may be changed.

### 3.1. Film thickness 500–2000 Å

In the first system, in which the silver film was 500–2000 Å, we have found that there are two different situations.

(1) In cases where the Hg droplet was deposited on the Ag film right after the evaporation, we observed two interfaces (Fig. 2).

(i) The first front, which has a smeared interface, is apparently a solid solution of mercury in silver. As the silver is very clean the surface tension forces drive the mercury on the silver very fast ($\approx$ 5 μm/s) and hence, there is not enough time for the mercury to react with the surface. This may also explain the small (400 Å) thickness of this front (AFM) (Fig. 3a). In addition, the optical properties of this front, i.e., brightfield, darkfield and DIC images were the same as the properties of the silver itself – another indication of a solid solution. In this case, there is no sharp line but a smeared one, which may be an indication of a strong wetting process in which diffusion plays an important role. It is impossible to associate an accurate and continuous line to this interface in order to determine the scaling exponents.
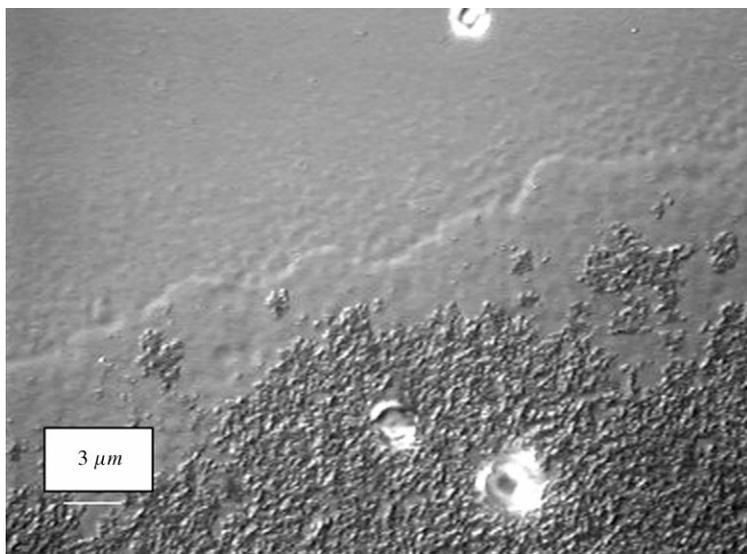
Fig. 2. A top view, taken by the optical microscope, in the middle ($t = 10$ min out of total 20 min) of the spreading process. The droplet size was about 150 μm and the thickness of the clean surface silver film was 2000 Å.

(ii) The second front (Fig. 2), which is about 500 Å higher than the first one (Fig. 3b), is due to the growth of a new inter-metallic phase inside the solid solution. When the solid solution becomes saturated a phase transition to a new inter-metallic compound ($Ag_4Hg_3$) takes place. This phase grows in the solid solution in a structure of islands (Fig. 4) that can be explained by mechanisms of nucleation and growth. Fig. 4 shows the same zone in two different times, and the interval between them is 1 sec. The grains of the new phase are more likely to grow next to other grains due to the surface and volume free energy difference so that a shape of an interface is formed. However, it was difficult to draw a continuous line along this interface, because the interface itself was not continuous.

(2) In cases where the Hg droplet was deposited on the Ag film about three days after the evaporation, we observed only one front (Fig. 3c). The Ag surface became contaminated during this time and its surface tension coefficient had been changed. Thus, the large driving forces had been reduced, and the velocity of spreading had also reduced by a factor of two. Therefore, the chemical reaction process was probably faster than the wetting process and the two fronts (of the previous case) coincided. We have also compared the interface during the spreading process to the interface at the end of the experiment (Fig. 5). In both cases the interface is well defined and one can draw a continuous line along it. Notice the difference between the pictures – the upper one is less smooth and hence the roughness exponent is expected to be smaller. It is also clear that there is no self-affinity in the lower picture (different views for different lengths), and hence we expect a cross-over in the roughness exponent value.
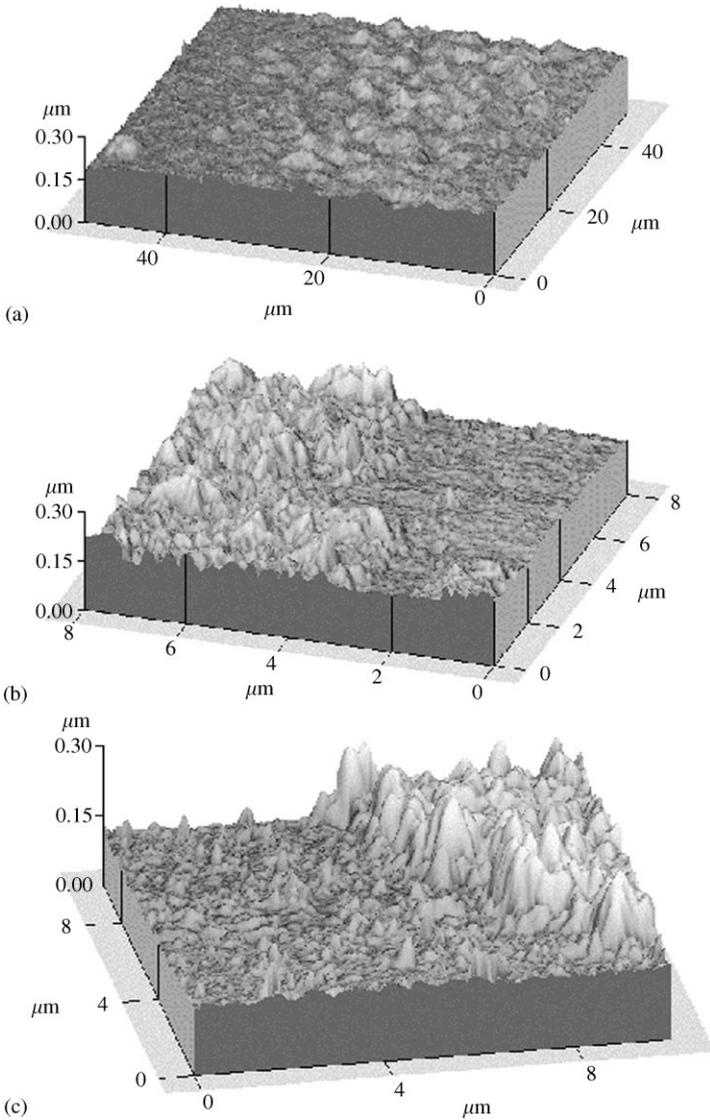
Fig. 3. A three-dimensional view, provided by AFM, taken several days after the spreading experiment. The direction of spreading is from right to left in the upper (a) and (c) lower pictures, and from left to right in the middle one (b). More details and explanations are given in the text.

The grains along the interface of the lower picture belong to the new phase of the mixture between the two compounds. Since the upper picture was taken during the experiment, where the diffusion is dominant, we could not find these grains there.

In order to calculate the exponents $\alpha$ and $\beta$ using Eqs. (1) and (2) we have first measured the interface's width, $W$. We observed that $W$ grows only for about 10 sec and then saturates to a maximal $W_m$ of about 5 μm. At a typical time
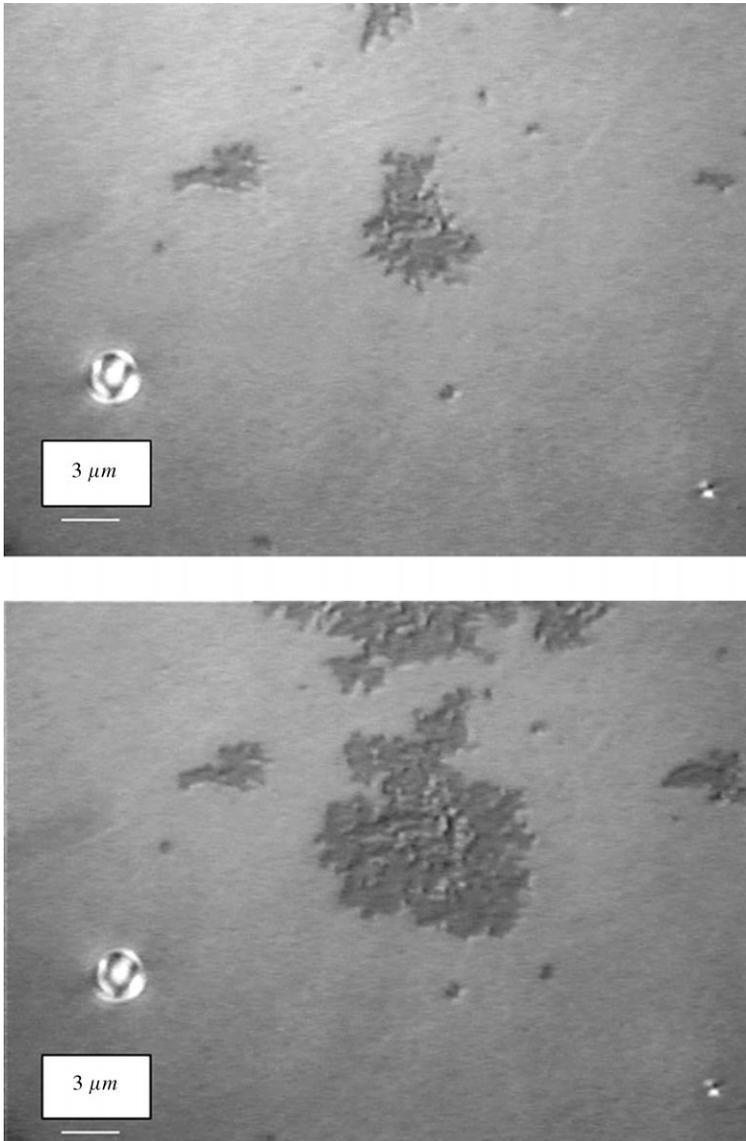
Fig. 4. The two pictures show the same zone in two successive times, 1 sec apart. The pictures were taken in the beginning ($t = 2$ min out of total 20 min) of the spreading process.

during the experiment ($t = 10$ min out of total 20 min), we found $\alpha = 0.66 \pm 0.03$ and $\beta = 0.46 \pm 0.02$ (Fig. 6a and b), which satisfy the scaling law

$$\alpha + \alpha/\beta = 2 \tag{3}$$

within the error bars. The relatively low value of $\beta$, compared, for example, with values obtained in related experiments [10], $\beta = 0.68 \pm 0.04$, is probably due to de-wetting forces
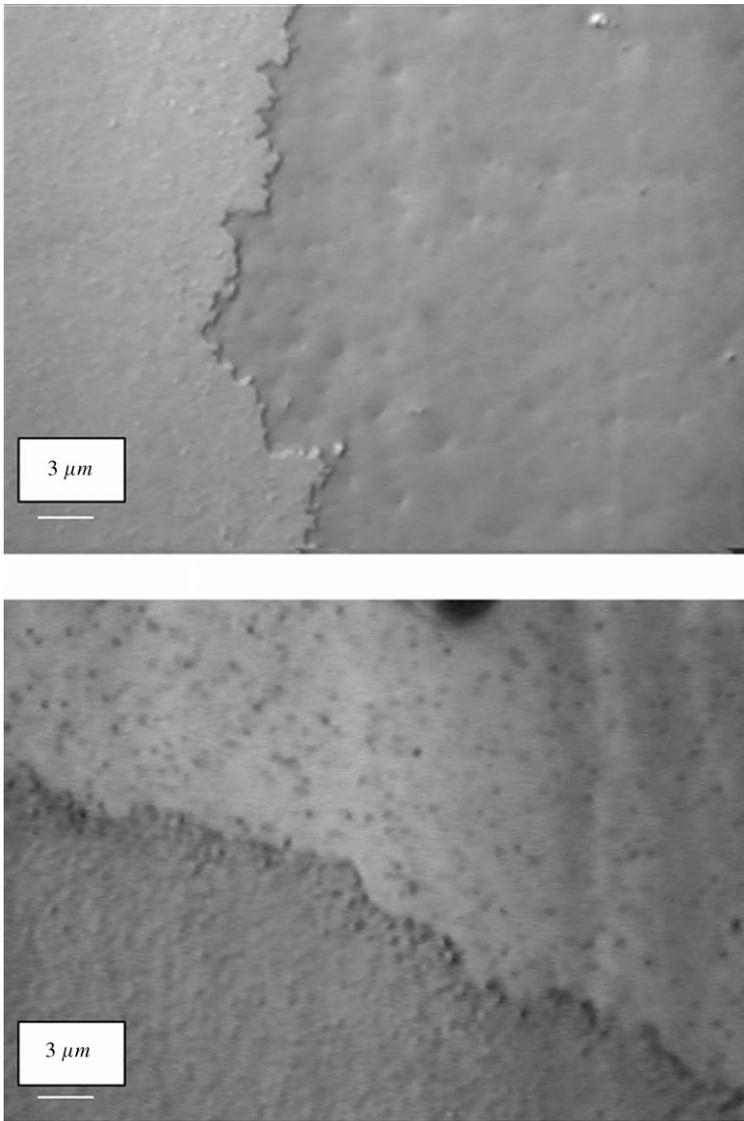
Fig. 5. The interface between the silver and the mercury in the case where the silver was exposed to the air. The upper picture shows the interface during the experiment while the lower one shows the interface at the end of it. Direction of spreading is from right to left in the upper picture, and bottom to top in the lower one. The droplet size was 150 μm and the thickness of the silver was 2000 Å.

or chemical reactions. However, when the spreading process has completely stopped we have calculated $\alpha$ again and found that $\alpha = 0.76 \pm 0.02$ for short ($L < 2$ μm) length scales (small $L$), and $\alpha = 0.47 \pm 0.02$ for long length scales (large $L$), (see Fig. 6c). The high value of $\alpha$ ($\alpha \approx 0.76$) does not obey the scaling law $\alpha + \alpha/\beta = 2$ since the isotropic assumption on which this relation is based [5] is no longer relevant. The
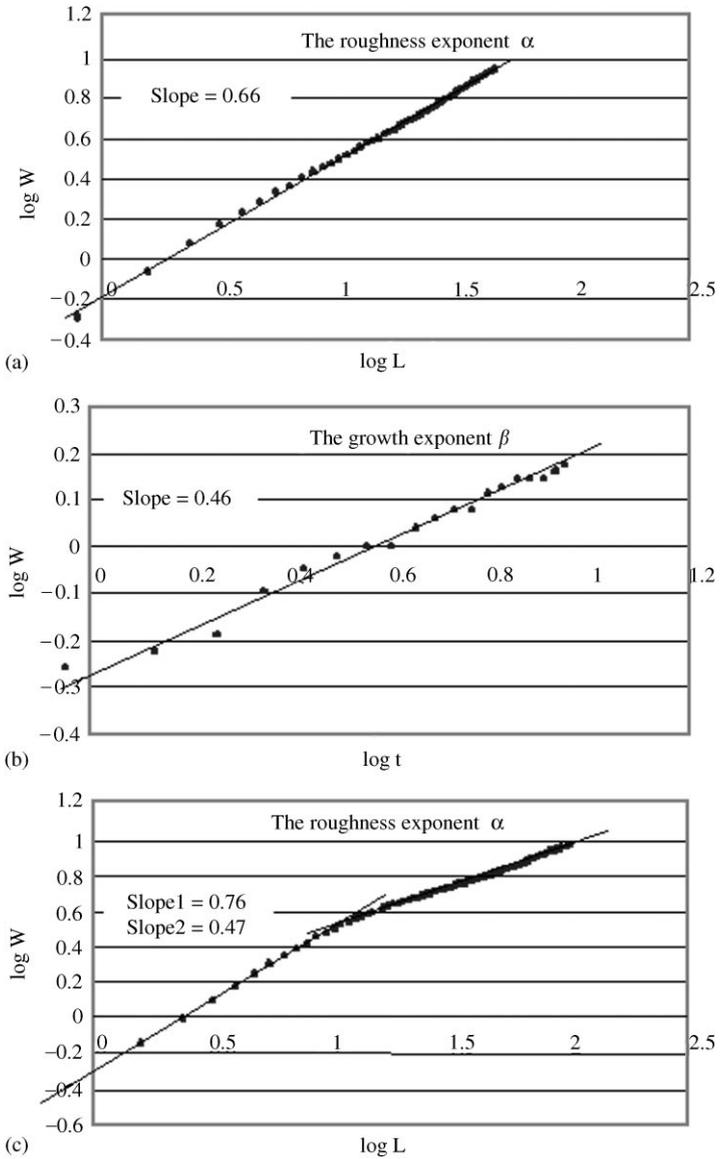
Fig. 6. The roughness (a) and growth (b) exponents calculated from experimental data in the thinner system (Ag thickness 2000 Å, and Hg diameter 150 μm). (c) shows the cross-over behavior of the roughness exponent at the end of the experiment.

strong correlation in short scales is probably due to the chemical reaction – grains of the new phase tend to grow next to other grains due to the surface and volume free energy differences and thus, one can observe a strong correlation in short scales. The value $\alpha \approx 0.47$ for long-length scales is in good agreement with the KPZ theory [11].
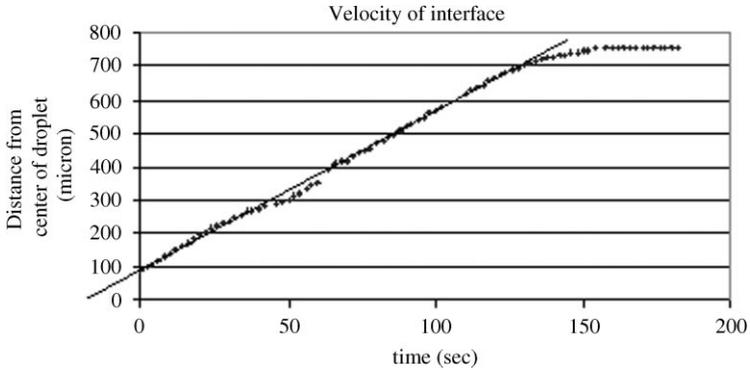
Velocity of interface



Fig. 7. This figure shows the distance of the interface from the center of droplet vs. time, in the thinner system. The velocity is given as the slope $v = dx/dt = const \approx 4.5 \, \mu m/s$.

We have also found that there is no effect of the droplet size or the silver thickness on the scaling exponents. However, the quality of the surface of the silver does play an important role since (i) it influences the velocity of the interface, (ii) it determines the number of fronts and (iii) it determines the final structure, chemical and optical, of each front. Since the silver is contaminated only at the very top of it ($\approx 20$–$30$ Å), it is obvious that the relevant processes take place on top of the silver and not too deep inside.

The velocity of each of the interfaces was also measured, and it was found that $x \approx t$ (Fig. 7) along 80% of the spreading process. The fact that $v = const$ ($\approx 2$–$5 \, \mu m/s$), is probably due to the large driving forces [4] stemming from the high surface energy of the silver ($\approx 1200 \, erg/cm^2$) [12]. The different quality of the silver surface determines only the specific value of the velocity but not its time dependence, and the droplet size has no effect on the velocity whatsoever.

## 3.2. Film thickness 0.1 mm

In this system (silver thickness is 0.1 mm) we have observed only one case in which there are two different fronts. However, the optical, physical (and probably chemical), structures of the fronts are different from those we obtained in the thinner film system. At the beginning, the droplet starts to spread on the silver and only one front is observed. This front is relatively wide ($\approx 1 \, \mu m$), made of pure Hg (bulk), its interface is extremely straight, and thus indicates a wetting process. After a while (20 sec) a new front is suddenly observed. This front, which is apparently a thin (600 Å by AFM) Hg layer that wets the surface, moves a little faster than the previous one, which then slows, and probably creates a solid solution on top of the Ag layers. This new front develops a rough interface, and its fluctuations continue to grow for about 5 min with a maximal $W_m$ of about $W \approx 50 \, \mu m$. The scaling exponents measured and calculated in this system are only for this (the new and outer) front and they were found to be: $\alpha = 0.77 \pm 0.04$ and $\beta = 0.6 \pm 0.02$. These exponents, although very

much different from the thin film exponents, still obey the scaling relation $\alpha + \alpha/\beta = 2$. Similar exponents have been obtained in Ref. [9]. When the spreading process stopped (after 5 min), we have found that $\alpha \approx 0.82$ for short ($L < 8$ µm) length scales (small $L$), and $\alpha \approx 0.5$ for long-length scales (large $L$). This cross-over phenomenon is quite similar to the thin film system but the correlation length $L$ is larger probably due to the larger bulk of the silver, and due to different chemical reaction processes that stem from different granular surface structures.

## 4. Summary

To summarize, we have presented an experimental system, which is governed by different mechanisms on different time and length regimes: wetting and diffusion at early stages and chemical reaction at final stages and short-length scales. This observation results from our calculations of the roughness and growth exponents of the interface. In addition, by comparing exposed and non-exposed specimens, we have found that the process takes place only on the surface and not too deep inside. Moreover, we have found that the Hg droplet size and even gravity did not affect the scaling exponents, or the front velocity.

## Acknowledgements

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