Complex Patterns in Reactive-Wetting Interface Dynamics

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Imbibition in Disordered Media

- Oil recovery - displacement of a liquid by another
- Printing Processes – ink penetration in paper, coating of paper
- Food Industry – cooking, wine filtering
- Biological Sciences – fluid transport in plants, water imbibition into seeds, water penetration into soils, medical applications
- Surface Chemistry – contact angle, droplets on surfaces
- Composite Materials - metal in fiber, metal-metal composites
- Textiles – behavior of garments in the presence of liquids
- Construction - water penetration into concrete or cement pastes

Different length and time scales! Universality?!
Outline

• Introduction

• What is reactive-wetting?

• Where are the Complex Patterns?
  - Spatio - The Correlation Length
  - Temporal - The Persistence Measure

• Continuous fluid invasion model (?)

• Summary
Hg-Ag (Au) Reactive-Wetting in Room Temperature

Side-view

Glass

Ag, Au 1000A-0.1mm

Hg 100μm

Optical microscope + DIC
CCD Camera

Top-view

Hg
Ag, Au
Silver 4200A

Bulk Spreading

Kinetic Roughening

t = 5 sec

50μm

t = 10 sec

t = 15 sec
Dynamics of Classical Wetting

Side view

Tanner’s Law

\[
\begin{align*}
\theta(t) & = t^{-3/10} \\
R(t) & = t^{1/10} \\
H(r=0,t) & = \frac{1}{2} R(t) \theta(t)
\end{align*}
\]

Reactive wetting?
Droplet placement

Spreading & reaction

Touching the glass

Halo – fast flow

Final stage
Dynamical 3-D Shape Reconstruction

Side View from a Top View!

Be’er & Lereah, JOM 2002
Silver 4200 A

$t=5, 15, 25$ sec
Silver 4200 A

Bulk spreading

Halo

θ(deg)

contact angle

step

R(μm)

droplet radius

R ~ t

time (sec)
Final stage – Top-view

SEM

Ag₃Hg₄
Ag₄Hg₃
Complex Patterns

Kinetic Roughening of the Reaction Band

Screen height - about 100µm

Ag thickness = 0.1 mm (foil)
Hg initial radius - about 150 µm.
Bulk height from surface - about 1 µm.

Initial time here is 15 sec
Total time of experiment = 5 min
Complex Patterns

Hg \approx 150 \mu m
Ag \approx 4000 \AA

Glass
Reactive-Wetting in High Temperature

Sn spreading on 1μm Au-coated 12μm Cu  (Singler et al 2008)
Patterns in Biology

Bacterial Colonies Growth - Eshel Ben-Jacob

Dynamics and Pattern Formation in Invasive Tumor Growth

Evgeniy Khain and Leonard M. Sander

FIG. 1. Growing tumor spheroids from in vitro experiments [5] in collagen gel for the wild-type (a) and mutant (b) cells. These

FIG. 4. Gray scale representation of the cells density for isotropic \((p = 1\), the right panel) and anisotropic \((p = 0.3\), the left and center panels) diffusion, computed numerically from Eq. (2).
In isotropic systems

\[ W^2(L,t) = \langle h(x,t)^2 \rangle - \langle h(x,t) \rangle^2 \]

Family-Vicsek scaling

\[
W(L,t) \approx \begin{cases} 
  t^\beta & t << t_0 \\
  L^\alpha & t >> t_0 
\end{cases}
\]

\[ t_0 \propto L_0^{\alpha/\beta} \]

\( \beta \) - growth

\( \alpha \) – roughness

In isotropic systems

\[ \alpha + \alpha/\beta = 2 \]
\[ W^2(L, t) = \langle h(x, t)^2 \rangle - \langle h(x, t) \rangle^2 \]
Scaling Exponents
Silver 2000 A

The growth exponent $\beta$
Slope = 0.46

The roughness exponent $\alpha$
Slope1 = 0.76
Slope2 = 0.47

Correlation Length

$\beta = 0.46 \pm 0.02$

$\alpha = 0.76 \rightarrow 0.47$

Crossover behavior
## Summary of Results

<table>
<thead>
<tr>
<th>Material</th>
<th>Thickness</th>
<th>$\alpha$</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silver</td>
<td>2000A</td>
<td>0.76 ± 0.03</td>
<td>0.46 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>0.1mm</td>
<td>0.82 ± 0.04</td>
<td>0.60 ± 0.02</td>
</tr>
<tr>
<td>Gold</td>
<td>1500A</td>
<td>0.85 ± 0.03</td>
<td>0.76 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>3000A</td>
<td>0.86 ± 0.04</td>
<td>1.00 ± 0.04</td>
</tr>
</tbody>
</table>

Universality Class ??

$\alpha + \alpha/\beta = 2$

NOISE – 
Substrate Roughness

Correlation length

- 2µm
- 8µm
- 7µm
- 14µm
Single Interface: Temporal Width Fluctuations

Silver foil 0.1 mm

Width

Log $W$ (µm)

$\beta=0.60$

$L=25\mu$m

$L=3\mu$m

Log $t$ (sec)

time
Non Monotonic Width Growth
Competition scheme

QKPZ equation:

\[ \frac{\partial h}{\partial t} = F + \nu \nabla^2 h + \frac{\lambda}{2} (\nabla h)^2 + \eta(x, h) \]

Surface tension  Non-linear growth  Noise
New measure:

$$\varphi^2 = \left\langle (\log w_i - \log w_{linear})^2 \right\rangle_i$$
Fluctuations and the Correlation Length

- Correlation Length from Interface Fluctuations
- Correlation Length from Roughness Exponent ($\alpha$)
Simulation Results

a single interface: width fluctuations!

\[ \beta = 0.599 \]
• Maximum - competition between non-linear growth ($\lambda$) and surface tension ($\nu$).
Average Over Many Interfaces

Fluctuations disappear when the interface is averaged!
Thin Gold Films

1500-3000Å

d=1500Å

$L_c=8\mu m$

Width Fluctuations

Crossover Length from Interface Fluctuations

Crossover Length from Roughness exponent
Water Spreading on Paper
Family et al (1992)

$d = 1500 \text{A}
L_c = 18 \text{ pix} = 9 \text{ mm}$

Width Fluctuations

Crossover Length from Interface Fluctuations

Crossover Length from Roughness exponent
Silver – 2000 Å

Average pin height – 200 Å
Average pin width – 1000 Å

Gold – 1500 Å

Average pin height – 100 Å
Average pin width – 500 Å

Silver foil 0.1 mm

Average pin height – 250 Å
Average “row” distance – 10000 Å
Effect of substrate surface roughness
Patterns using lithography

Isotropic

Anisotropic

Roughness exponent $\alpha$ always around 0.8
• Initial thickness of the silver substrate 4000 Å
• Different depth 500-2000 Å with intervals of 500 Å

* Movie 2 slower velocity than for “smooth” surfaces
• Spreading along the channel's direction - 'fingers' like shape.

* Movie 3

Channel’s width: 4μm.
Channel’s depth: 2000Å.

Channel’s width: 40μm.
Channel’s depth: 2000Å.
Spreading *perpendicular to* the channel's direction - velocity jumps between two values.

Channel width: 20μm

Channel width: 4μm

* Movie 4

Channel’s width: 20μm. Channel’s depth: 2000Å.
<table>
<thead>
<tr>
<th>T=25°C</th>
<th>T=15°C</th>
<th>T=10°C</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td><img src="image3.png" alt="Image" /></td>
</tr>
</tbody>
</table>

**Temperature Effect**

-15 < T(°C) < +25
Temperature Effect

\(-15 < T(C) < +25\)

\[ \beta \text{ increases with } T \]

\[ \alpha = 0.8 \text{ constant} \]
What really happens in the growth regime???
The persistence measure

- Persistence probability $P(t)$ is the probability that a certain fluctuative variable never crosses a chosen reference level within time interval $t$.

Universal scaling form: $P(t) \propto t^{-\theta}$

Derrida et al. PRL (1994)
Persistence in Reactive-Wetting Interface

- Fluctuative variable: "location" of points on interface
- Reference level: height at time $t_0$
Survival - the algorithm

- Single point – distance from $<h>$ vs. $t$
- Divide $t$ axis to intervals in length $t'$ where $t'=1,2,...T_{\text{max}}$ sec
- Count “persistent” intervals for each $t$.

Constant reference level - $h^*=0$

$S(x,t_0,t_0+t)$ is prob.
that sign[$h(x,t_0+t')$]
remains the same for all $0 \leq t' \leq t$

Average over $t_0$ & $x$:

$P(t)$ - Power Law decay

$S(t)$ - Exponential decay

C. Dasgupta et. al.
Persistence Exponent Results

- Ising model (PRL 1996)
  \[ \theta = 0.37, 0.22, 0.26 \] (1d, 2d, 3d)

- Potts model (Physica 1996)
  \[ \theta = 0.86 \] (2d- large q)

- Random walk (PRE 1997)
  \[ \theta = 0.5 \]

- Linear Langevin equations (PRE 1997)

- KPZ equation (Europhys. Lett. 1999)
  \[ \theta_+ = 1.18 \quad \theta_- = 1.64 \]
Experimental results

- 2d Liquid crystal (PRE 1997)
- Fluctuating monatomic steps on crystal (PRL 2002)
- Combustion fronts in paper (PRL 2003)
- 2d Soap froth (PRL 1997)

Relation $\theta = 1 - \beta$ is valid even though system is non-linear.

$\theta = 0.77 \pm 0.03$

$\theta = 0.66 \pm 0.03$

$\theta = 0.88 \pm 0.02$
Results for Reactive-Wetting

- First time regime:
  - $W(t) \approx \text{const}$
  - $\theta = 0.55 \pm 0.05$

- Random walk

- Persistence in growth regime $\rightarrow$ new calculation!
Persistence – growth regime

- \( \beta = 0.68 \pm 0.07 \) , \( \theta = 0.37 \pm 0.05 \)

- Relation \( \theta = 1 - \beta \) is valid: \( \theta + \beta = 1.04 \pm 0.08 \)
 Persistence – saturation regime

Random walk again: \( \theta = 0.47 \pm 0.01 \)

\[ y = -0.4829x - 0.2152 \]
\[ R^2 = 0.9617 \]
Global interpretation

-1.5 -1 -0.5 0 0.5 1 1.5 2
-0.35 -0.15 0.05 0.25 0.45 0.65 0.85 1.05 1.25
log (t [sec])

L = 150 pix

log (w [pix])

log (P)

Noise

Surface tension

Non-linear growth

evidence: \( \theta \sim 0.5 \)
Persistence simulations

QKPZ

Whole experiment

\[ \theta = 0.76 \pm 0.006 \]

Ising

\[ \theta = 0.38 \pm 0.005 \]

Almost the same, but not like in the experiment!

Like the growth regime in experiment!
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Experiment</th>
<th>QKPZ sim.</th>
<th>Ising sim.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>$\alpha = 0.83 \pm 0.008$</td>
<td>$\alpha = 0.72 \pm 0.02$</td>
<td>$\alpha = 0.92 \pm 0.03$</td>
</tr>
<tr>
<td>$\beta$</td>
<td>$\beta = 0.68 \pm 0.07$</td>
<td>$\beta = 0.61 \pm 0.02$</td>
<td>$\beta = 0.33 \pm 0.01$</td>
</tr>
<tr>
<td>$\theta$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>first regime</td>
<td>$\theta = 0.55 \pm 0.05$</td>
<td>$\theta = 0.8 \pm 0.01$</td>
<td>$\theta = 0.38 \pm 0.005$</td>
</tr>
<tr>
<td>growth regime</td>
<td>$\theta = 0.37 \pm 0.05$</td>
<td>$\theta = 0.76 \pm 0.006$</td>
<td></td>
</tr>
</tbody>
</table>

First regime is not part of QKPZ process

Macroscopic behavior – QKPZ?

Microscopic behavior - Ising

Persistence exponent - Ising

Growth exponent - QKPZ
Persistence Summary

😊 Three kinetic regimes in experiment:
   😊 Transient regime - random walk mechanism
   😊 Growth regime - \( \theta + \beta = 1 \)
   😊 Saturation regime - random walk again

😊 Macroscopic - Growth: \( \beta = 0.68 \pm 0.07 \) - QKPZ

😊 Microscopic - Persistence: \( \theta = 0.37 \pm 0.05 \) - Ising
Summary

• What is reactive-wetting?

Side view from Top View
Bulk Spreading – $\theta(t)$, $R(t)$

• Where are the Complex Patterns?

Spatio - **Roughness Exponent**, Lateral Correlation Length
Temporal - **Growth Exponent**, The Persistence Measure

• Continuous fluid invasion model  
  (Hecht, HT – PRE 2004)
References

A. Be’er, Y. Lereah, I. Hecht, H. Taitelbaum, Physica A 302, 297 (2001)
A. Be’er, I. Hecht, H. Taitelbaum, Phys. Rev. E 72, 031606 (2005).
Calibration: colors (hues) vs. slopes

Resolution Limits

Time: 0.04 sec !!
(frame to frame interval)

Lateral: 0.5 μm
Slope: 1°
AFM studies - A few days later.…

First front - smeared - solid solution

Second front - 500 Å higher - inter-metallic phase
AFM studies  -  a few days later.....

contamination

Sharp, single front line
<table>
<thead>
<tr>
<th>$\alpha,\beta$</th>
<th>Equation</th>
<th>Description</th>
<th>Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta=1/2$</td>
<td>$\frac{\partial h(x,t)}{\partial t} = \eta(x,t)$</td>
<td>Particles fall randomly, and stick to the lower one.</td>
<td>RD</td>
</tr>
<tr>
<td>$\beta=1/4$</td>
<td>$\frac{\partial h(x,t)}{\partial t} = \nu \nabla^2 h(x,t) + \eta(x,t)$</td>
<td>Particles look for the lowest energy place.</td>
<td>RD+SR</td>
</tr>
<tr>
<td>$\alpha=1/2$</td>
<td>EW</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\beta=1/3$</td>
<td>$\frac{\partial h(x,t)}{\partial t} = \nu \nabla^2 h(x,t) + \frac{\lambda}{2} (\nabla h)^2 + \eta(x,t)$</td>
<td>Horizontal growth is possible.</td>
<td>BD</td>
</tr>
<tr>
<td>$\alpha=1/2$</td>
<td>KPZ</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\beta=1/2*$</td>
<td>$\frac{\partial h(x,t)}{\partial t} = \nu \nabla^2 h(x,t) + \frac{\lambda}{2} (\nabla h)^2 + \eta(x,h)$</td>
<td>The noise term depends on the location.</td>
<td>QKPZ</td>
</tr>
<tr>
<td>$\alpha=2/3*$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\beta=3/8$</td>
<td>$\frac{\partial h(x,t)}{\partial t} = -K \nabla^4 h(x,t) + \eta(x,t)$</td>
<td>Particles diffuse looking for preferred place.</td>
<td>MBE</td>
</tr>
<tr>
<td>$\alpha=3/2$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
## Scaling Exponents (T) So Far…

<table>
<thead>
<tr>
<th></th>
<th>$\alpha(T)$</th>
<th>$\beta(T)$</th>
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<tbody>
<tr>
<td>Cavalcanti et al</td>
<td>-</td>
<td>decreases</td>
</tr>
<tr>
<td>PRE 2004</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Das Sarma et al</td>
<td>decreases</td>
<td>decreases</td>
</tr>
<tr>
<td>PRB 2004</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ferreira et al</td>
<td>increases</td>
<td>increases</td>
</tr>
<tr>
<td>Appl. Phys. Lett. 2006</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zubimendi et al</td>
<td>no change</td>
<td>-</td>
</tr>
<tr>
<td>Langmuir 1996</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Survival - first prediction in 1962!

Zero Crossing Probabilities for Gaussian Stationary Processes

G. F. Newell; M. Rosenblatt


\[ S(t) \propto \exp\left(-\frac{t}{\tau_s}\right) \]
Persistence – simulation results

- **QKPZ exponent:** \( \beta = 0.61 \pm 0.02 \)
- **Persistence exponent:**
  - for whole time: \( \theta = 0.8 \pm 0.01 \)
  - for growth regime: \( \theta = 0.76 \pm 0.006 \)
Microscopic Approach—Fluid Invasion Model

Inbal Hecht and HT,
Motivation for new models:

✓ A continuous fluid invasion model.
✓ Experiments with $\alpha \approx 0.8$ are not explained.
✓ Different results for Wetting and Non-Wetting fluids.
Arcs Model – Cieplak & Robbins (PRL 1988)

Two dimensional array of disks, $L$ “atoms” per row / column

Initial interface: a ring of arcs, around the system center

The arc’s radius: $r = \gamma / P$

$\gamma$ - surface tension, $P$ - pressure

$\theta$ is the angle between the disk and arc.

Wetting limit: $\theta = 0^\circ$; Non-wetting limit: $\theta = 180^\circ$

Dynamics: Stepwise, Quasi-Static process

- The pressure is increased by a small amount (~1%).
- All arcs are updated according to the new radius.
- Unstable arcs are replaced by new arcs in the next stable position.
Instabilities of arcs and their removal:

➢ “Burst” – There is no arc with the given radius, intersecting these two disks with the given $\theta$.

➢ “Touch” – The arc intersects a third disk.

➢ “Overlap” – Two adjacent arcs intersect
Simulations

1. $\theta=10^\circ$.
2. $\theta=37^\circ$.

**Order of instability removal?**

1. TOB - Touch, Overlap, Burst (CR original model).
   - **Global** Surface tension is the main mechanism in the system.

2. TBO - Touch, Burst, Overlap – Better agreement with experimental results.
   - There is a strong **local** mechanism that is stronger than surface tension.

Do the wetting properties influence the interface roughness?
Does $\alpha$ change with $\theta$?
Instabilities Analysis - TOB Model

Inconsistent!

Increase in the number of Bursts that occur
The number of treated Bursts is unchanged!
Instabilities Analysis - TBO Model

(a) occurrence

(b) treatment

consistent!
Roughness Exponent $\alpha$ - TOB Model

$\alpha \sim 0.7$, independent of $\theta$ – same $\alpha$ for different fluids.

Unlike experimental results: $\alpha=0.81$ for glycerol but $\alpha=0.88$ for water.

for $\theta > 50^\circ$ the interface is fractal.
Roughness Exponent $\alpha$ - TBO Model

- for $\theta < 28^\circ$, $\alpha \sim 0.65$ and constant.
- for $28^\circ < \theta < 50^\circ$, $\alpha$ grows monotonically with $\theta$.
- for $\theta > 50^\circ$, the interface is fractal.