Simple ideas on …

Pinning and Depinning Mechanisms

Coupling between evaporation-induced deposition and moving contact lines

Hugues Bodiguel
Capillary flow as the cause of ring stains from dried liquid drops

Robert D. Deegan, Olgica Bakajin, Todd F. Dupont, Greb Haber, Sidney R. Nagel & Thomas A. Witten

When a spilled drop of coffee dries on a solid surface, it leaves a dense, ring-like deposit along the perimeter (Fig. 1a). The coffee—initially dispersed over the entire drop—becomes concentrated into a tiny fraction of it. Such ring deposits are common wherever drops containing dispersed solids evaporate on a surface, and that influence processes such as coating, painting and...
Universality of rings?

Successive pinning and depinning

Adashi et al, Langmuir 1995

Wide types of final deposit: Pinning is not universal.

Bhardwaj et al, Langmuir 2010
Evaporating droplets

Depinning occurs at a fixed contact angle ($\sim 35^\circ$)

Just after depinning, the contact angle recovers its ‘equilibrium’ value


Pinning force

- ‘unbalanced Young equation’

The deposit support a force due to the unbalanced Young equation

\[
F_{CL} = \gamma \Delta \cos \theta
\]

During the drying of a droplet, the force increases due to mass loss.

But the deposit is growing!

The deposit is able to compensate \( F_{CL} \) …

but could (probably) support a greater force \( \Rightarrow F_p \)!

**PINNING if** \( F_p > F_{CL} \)
Effect of contact angle value

High contact angle:
- the pinning force grows slowly
- but the evaporation tends to uniformity

Concentration also matters!  

**Strong coupling between solute accumulation and pinning**

*Cite sources*:

**Kuncicky and Velev, Langmuir 2008**
Moving contact lines

- Drying of a droplet:
  Contact line (CL) velocity $\sim \frac{dR}{dt}$
  
  Order of magnitude (water droplet at room temperature): 1 $\mu$m/s
  CL velocity (in absence of pinning) is imposed by the evaporation

- Dip-coating
  CL velocity: free parameter
  
  Expected competition between the CL pinning and the ‘imposed’ CL movement
Moving contact lines

Advancing contact lines

![Diagram of advancing contact lines](image1)

Receding contact lines

![Diagram of receding contact lines](image2)

In both cases, the velocity field in the CL region is governed by the evaporation

\[ J_0 x^{-1/2} \]

ie for

\[ x \ll \left( \frac{J_0}{U\theta} \right)^2 \]

Balance of capillarity / viscous drag in presence of evaporation:

\[ \theta_M^3 = \theta_e^3 - 9\text{Ca} \ln \left( \frac{L}{a} \right) + \frac{24\eta J_0}{\gamma \theta_e a^{1/2}}. \]

Berteloot et al, EPL 08

For pure liquids, the contact angle remains roughly unchanged at low Ca
1. Solute deposition and accumulation

2. Pinning: deposit-CL interaction

3. Stick-slip phenomena: successive pinning and depinning
1. Solute deposition and accumulation
Experimental set-up

Control parameters:
- Displacement of the contact line by pumping liquid from the reservoir
  \[0.5 \mu m/s < V < 2 \text{ mm/s}\]
- Control of evaporation rate via humidity, temperature and air flow
  \[0.3 \mu m/s < v_{ev} < 3 \mu m/s\]
- Volume fraction of solute (silica particles or polymer).
  \[0.1 \% < \phi < 20 \%\]

Measurements:
- Monitoring of contact line displacement by digital camera (accuracy \(\sim 2 \mu m\)).
- Deposit structure studied a posteriori by optical profilometry, AFM and SEM.
Coating regimes: influence of the velocity (colloidal suspension)

System: silica particles in water
Diameter: 80 nm

Colloidal suspension – $v_{ev} = 0.4 \, \mu m/s$

Velocity $V$

- periodic patterns
- stick-slip
- ‘uniform’ deposition
- steady velocity

1-10 \, \mu m/s
Coating regimes: influence of the velocity (colloidal suspension)

Colloidal suspension – $v_{ev} = 0.4 \mu m/s$

Velocity $V$

$\phi = 1.4\%$

$V = 200 \mu m/s$

1-10 \mu m/s

periodic patterns
stick-slip

‘uniform’ deposition
steady velocity

50 \mu m

1 \mu m
Coating regimes: influence of the velocity (colloidal suspension)

- **Colloidal suspension** – $v_{ev} = 0.4 \, \mu m/s$
- **Periodic patterns**: $\phi = 1.4\%$, $V = 20 \, \mu m/s$
- **‘Uniform’ deposition**: $\phi = 1.4\%$, $V = 50 \, \mu m/s$
- **Stick-slip region**: $V = 1-10 \, \mu m/s$

**Velocity $V$**
Coating regimes: influence of the velocity (colloidal suspension)

\[ \phi = 1.4\% \]
\[ V = 8 \mu m/s \]

Colloidal suspension – \( v_{ev} = 0.4 \mu m/s \)

Velocity \( V \)

periodic patterns
stick-slip

'uniform' deposition
steady velocity
Coating regimes: influence of the velocity (colloidal suspension)

**AFM measurement**

- \( \phi = 1.4\% \)
- \( V = 1 \, \mu m/s \)

**Optical profilometry**

- \( \phi = 2.4\% \)
- \( V = 5 \, \mu m/s \)

**Colloidal suspension** – \( \nu_{ev} = 0.4 \, \mu m/s \)

**Periodic patterns**
- stick-slip

**‘Uniform’ deposition**
- steady velocity

**Velocity** \( V \)
Measurement of deposit mean thickness

**Optical profilometer**

*Colloidal suspension*

\[ \phi = 4.9\% \]
\[ V = 15 \text{ \( \mu \text{m/s} \)} \]
\[ v_e = 0.42 \text{ \( \mu \text{m/s} \)} \]

**SEM**

*Colloidal suspension*

\[ \phi = 0.14 \% \]
\[ V = 30 \text{ \( \mu \text{m/s} \)} \]
\[ v_e = 0.42 \text{ \( \mu \text{m/s} \)} \]
Effect of control parameters on deposit mean thickness

Colloidal suspension

$V = 0.2 \, \mu m/s$ to $2 \, mm/s$
$\phi = 0.14\% \rightarrow 4.9\%$
$v_{ev} = 0.28 \rightarrow 0.42 \, \mu m/s$

$V = 0.5 \, \mu m/s$ to $1 \, mm/s$
$\phi = 0.47\%$
$v_{ev} = 0.28 \rightarrow 3 \, \mu m/s$

Jing et al, Langmuir 2010
Experimental scaling laws

Colloidal suspension

Rescaling: \( e_d^* = e_d / (\phi v_e) \)

For \( V < 100 \, \mu m/s \):

\[ \frac{e_d V}{\phi v_e} \approx 330 \, \mu m \]

Jing et al, Langmuir 2010
Simple model for low velocity regime

Main assumptions:
- 2 domains: solid ($\phi(x) > \phi_g$) and liquid ($\phi(x) < \phi_g$).
- Steady regime.

Global mass balance: \[ Q(L_0) - h_0 V = Q_{evap} = L v_{evap} \]

Solute mass balance: \[ \phi_g h_0 V - \phi_0 Q(L_0) = 0 \]

\[ e_d = \phi_g h_0 = \frac{\phi_0}{\phi_g - \phi_0} \frac{v_{evap} L}{V} \]

\[ \frac{e_d V}{\phi_0 v_{ev}} \approx L \]

Quantitative agreement !!!
Influence of the rheology?

- **Colloidal suspension**
  - Silica particles in water
  - Diameter: 80 nm
  - Glass transition: $\phi_g \sim 0.64$

- **Polymer solution**
  - Polyacrylamide/water
  - $M_w = 22$ kg/mol or $M_w = 5000-6000$ kg/mol
  - Glass transition: $\phi_g = 0.74$
Comparison with polymer solutions

Polymer solutions

\[ e^*_d = e_d / (\phi v_{ev}) \]

- Same results with polymer solution and colloidal suspension
- No effect of viscosity !!!

Jing et al, Langmuir 2010

\[ v_{ev} = 0.28 \, \mu m/s \]
Regime at low velocity

**Evaporative regime:**

- No effect of the solute characteristics (colloid or polymer)
- No effect of the viscosity
- Flow driven by evaporation:

\[
e_d = \frac{\phi_0 v_{ev} L}{\phi_g V}
\]

\[v_{ev} = 0.28 \text{ to } 0.42 \mu m/s\]
Universality of the evaporative regime

Polymer, colloid, but also phospholipids

... *Le Berre et al, langmuir 09*

Different geometry, but again, the length involved is the meniscus size

High velocity regime

Landau-Levich film ...
Different regimes as a function of contact line velocity

\[ v_{ev} = 0.28 \, \mu m/s \]

(I) Evaporation regime

(II) Transition regime?

(III) Dynamical wetting

\[ \theta_E \approx 10^\circ \]

\[ Ca_c = 5.10^{-5} \]

\[ V_c \approx 3 \, mm/s \]

\[ \frac{e_d}{\phi} = 0.67 \, eCa^{2/3} \]

In our experiments:

\[ 4.10^{-9} < Ca < 3.10^{-5} < Ca_c \]
Simulation results

Transport equation
- In the gaz phase
- In the liquid phase
- Activity $a(\phi)$
- Viscosity $\eta(\phi)$

Doumenc and Gerrier, *under review*

Very good quantitative agreement
Preliminary conclusions

- Deposit size in steady state
  Main consequence:
  During the steady state, the deposition rate is constant and independent on the velocity!!!

$$\frac{d}{dt} \text{Deposit volume} = \phi_0 L v_{evap}$$

=> evaporative regime is a quasi-static regime

- Deposit growth during the pinning
  What happens just after the pinning?
  Should the steady state hypothesis be removed?
Deposit growth during the pinning

Simplified model

Uniform concentration at \( t=0 \) : \( \phi_0 \)

Particles conservation

\[
\phi_0 \theta x_i^2 = \phi_g \theta x_0^2
\]

Total flux due to evaporation :

\[
\theta x u(x) = J_0 x^{1/2}
\]

\[
\frac{dx}{dt} = \frac{J_0}{\theta} x^{-1/2}
\]

\[
x_i \propto t^{2/3}
\]

\[
x_0(t) \simeq \sqrt{\frac{\phi_0}{\phi_g}} \left( \frac{J_0 t}{\theta} \right)^{2/3}
\]

See also for a complete analytical solution: Zheng, EPJE, 2009

Berteloot et al, under review

Detailed calculation :

\[
x_0(t) = \left( \frac{\frac{x_0}{\theta}}{\frac{1}{3} \left( \sqrt{\frac{\phi_0}{\phi_g}} - \frac{1}{3} \left( \sqrt{\frac{\phi_0}{\phi_g}} + \sqrt{\frac{\phi_0}{\phi_g}} \right) \right) \right)^{3/2} t^{3/2}
\]
Deposit growth during the pinning

Experimental verification
drying of a droplet, 50 nm fluorescent particles 1% in water

Maximum intensity is proportional to the distance of the edge

Short time scalings verification for a drying droplet (initial concentration field is homogeneous)

Bertheloot, PhD thesis
Deposit growth during the pinning

For dilute suspensions:

- **Transient deposition regime:** Deposit volume $\approx \phi_0 L^{2/3} (v_{\text{evap}} t)^{4/3}$

  Main assumptions:
  - no Marangoni flow
  - $\text{Pe}_x >> 1$
  - $\text{Pe}_z << 1$
  - uniform initial volume fraction
  - the deposit shape is fixed by the corner contact angle

- **Steady state:** Deposit volume $\approx \phi_0 L v_{\text{evap}} t$

  This scaling is obtained with similar arguments, but with the steady state concentration field.

**What about stick-slip experiments?**
**What is the concentration field after the slip?**
Deposit growth during the pinning

- Validity range of the short time scaling?

\[ \phi_0 = 0.33 \phi_c \]
\[ \phi_0 = 0.1 \phi_c \]

From Zheng, EPJE 2009

The 2/3 exponent is limited to very short deposit
=> A concentration gradient is obtained rapidly
Concentration field

Concentration field measured using confocal microscopy

Bodiguel and Leng, under review

See poster for experimental details

Zheng's analytical solution (diffusion limited evaporation)

Incompressible particles?

Marangoni flows?

qualitative agreement but …
Some preliminary conclusions on solute deposition

Some conclusions on solute deposition:

Established results
- Steady state:
  - constant quasi-static universal deposition rate at low Ca: \( \phi_0 L v_{evap} \)
  - Standard LL regime at high Ca
- Transient regime from a uniform concentration
  - Increasing deposition rate at (very) short times: \( \phi_0 L^{2/3} v_{evap}^{4/3} t^{1/3} \)

Open questions
- Influence of Marangoni stress not clear for intermediate Ma
- Influence of colloidal interactions
2. Contact line pinning
Origin of the pinning force

De Gennes, Rev. Mod. Phys. 1985

- It is the local contact angle that matters!!!
CL interaction with the ‘imperfect’ surface

Advancing contact line on a negative slope

\[ F_p = \gamma (\cos(\theta + \alpha) - \cos \theta) \simeq -\gamma \sin \theta \alpha \]

Advancing contact line on chemically heterogeneous surface

\[ F_p = \gamma (\cos \theta_B - \cos \theta_A) \]

Cubaud and Fermigier, J Coll Inter 04

Ondarcuhu and PiedNoir, NanoLett 2005
CL interaction with the ‘imperfect’ surface

Receding contact line on a negative slope

\[ F_p = \gamma (\cos(\theta + \alpha) - \cos \theta) \simeq -\gamma \sin \theta \alpha \]

Receding contact line on a positive slope

unstable region
Consequences for depinning

- The deposit could support the following force

\[ F_p = \gamma (\cos (\theta_B(x, t) + \alpha(x, t)) - \cos \theta_A) \]

Physico-chemistry and roughness of the deposit

Local slope of the deposit

The exact position of the contact line is solution of:

\[ F_p(x, t) = F_{CL}(t) \]

Remark: receding contact angle instead of equilibrium one
Contact line pinning

- Flat substrate having a higher contact angle than the deposit:
  - PINNING of receding contact lines

- Flat surface having a lower contact angle than the deposit:
  - PINNING of advancing contact lines

- Deposit shape:
  - PINNING of both advancing and receding contact lines
Experimental validation

From in situ observation:

![Graph showing distance vs. time](image1)

![Photo with labels: Air Flow, pattern due to stick-slip, contact line movement, capillary growth](image2)

![Graph showing h - h₀ vs. time](image3)
Precise measurements of pinning force possible thanks to the capillary rise.

\[ E(h) = -\gamma \cos \theta \ h + \frac{1}{2} \rho gh^2 \]

\[ dE(h) = \left[ -\gamma \cos \theta + \rho gh \right] dh \]

**Pinning force**: \( F_{CL} = \gamma \Delta (\cos \theta) = \rho ge \Delta h \)

\( F_{CL} \sim 1 \text{ mN/m} \)

Precise measurements of pinning force possible thanks to the capillary rise.
Exemple of pinning force measurements

Decreasing velocities

When depinning occurs:

\[ F_{p_{\text{max}}} = F_{\text{CL}} \]
The pinning force is (for this system) of geometrical origin.

\[ F_p = \gamma \sin \theta_0 \alpha \]

Bodiguel et al, EPJ-ST 09
Other systems

- Deposit of higher contact angle

It should not pin the contact line, unless the geometry ...

Example:

Receding ethanol CL with Polystyren beads on glass…
Contact angle on PS : 60°
Contact angle on glass : 5°

Why is there pinning?

Geometry seems at first sight much lower than the contact angle difference!

Abkarian et al, JACS 2004

What is the effective receding contact angle?
Effective contact angle

The interface between the solid and the liquid is not sharp …
Is it possible to define the equivalent of an interfacial tension between a concentrated phase and a non concentrated one?

Monteux et al. Soft Matter 2008
Main assumptions of the macroscopic CL pinning interpretation:

- The deposit have to be considered as a new ‘solid’ substrate!
  - The deposit viscosity should be very high … static deposit!
  - The deposit needs to **stick** to the surface
  - **Sharp** transition from the concentrated zone to the fluid zone
  - Homogeneity along the CL direction (continuum view)
    => the deposit size is much higher than the particle size

Expected deviations:
- big particles or very small deposit
- viscous deposit
Big particles

- Big particles

Sangani et al., PRE 2009

Watanabe, Langmuir 2009
Some preliminary conclusions on pinning

- When the deposit size $>>$ solute size
  When the viscosity of the deposit is very high

*The pinning is similar to the CL pinning on an imperfect surface*
It thus depends on:
- Local geometry of the deposit (negative slope)
- Receding contact angle on the substrate …
  depends on solute volume fraction

Both are quantities that are usually unknown
Numerical simulations

Lagrangian framework
- Mass Transport
- Energy transport
- Velocity field

AND

- Mascropoic contact line pinning criterion

*Bhardwaj et al, New J. Phys. 2009*

See also: Uwe Thiele talk
3. Stick-slip phenomena

Depinning ...
3. Stick-slip phenomena

- Receding contact lines of colloidal suspension

- Advancing contact lines of colloidal suspension

- Polymer solutions
Receding contact lines

- Receding contact line
  - In situ systematic measurements of the pinning force

80nm silica particles

Depinning event:

De Gennes, Rev. Mod. Phys. 1985

Bodiguel et al, Langmuir 2010

Figure 4. Examples of pinning force measurements. The data have been horizontally displaced for clarity. From the top to the bottom, the corresponding imposed velocities are 20, 9, and 3.5 \( \mu \text{m s}^{-1} \). The weight fraction is 16\%, temperature 25 \( ^\circ \text{C} \), humidity 30\%, and \( v_{\text{vap}} = 0.4 \mu \text{m s}^{-1} \).
Receding contact lines

Empiric scaling:

\[ F_p \propto \frac{v_{ev} \phi}{V} \]
Receding contact lines

Strong stick-slip approximation (no slippage during the pinning)

\[
\begin{align*}
F_p &= \gamma \sin \theta_0 \alpha \\
F_p &\propto \frac{v_{ev}\phi}{V} \\
F_{CL} &= \rho g e \Delta h = \rho g e V_{t_{unpin}}
\end{align*}
\]

\[
F_{CL} = F_p \implies \alpha \propto \sqrt{v_{ev}\phi t_{unpin}}
\]

Bodiguel et al, Langmuir 2010
The exact contact line position is solution of:

\[ \gamma \sin \theta \partial_x \xi(x, t) = F_{CL}(t) \]

The amplitude of \( F_{CL} \) may change the shape of the deposit.

Coupling between the growing shape of the deposit shape and the exact CL position?
Direct measurement of the pinning time during the stick-slip:

Deposit volume (assuming steady state initial concentration)

\[ V(t) = \phi_0 L v_{evap} t \]

The pinning force is again an increasing function of the volume of the deposit…

\[ F_p(t) = \gamma \sin \theta \alpha(t) \]

\[ \alpha \propto \sqrt{V} \]

… independently on all experimental conditions!

Bodiguel et al, Langmuir 2010
Comment on Watanabe’s results

Very small deposit: limit of stick-slip!
Big particles …

Where is the limit between stick-slip and patterning?

Watanabe et al, Langmuir 2009

Width and spacing are proportional …
3. Stick-slip phenomena

- Receding contact lines of colloidal suspension
- Advancing contact lines of colloidal suspension
- Polymer solutions
Advancing contact lines

Strong stick-slip phenomenon

Advancing contact lines

➤ Model proposed:
Starting from the steady state, pinning occurs when the deposit thickness will become higher than 1 particle.

If we assume that the deposit rate is similar to that of receding CL:

\[ e_t \sim \frac{\dot{\phi}v_{evap}L}{U} \]

*Rio et al, Langmuir 2006*
Accumulation of solute at the contact line:
(hypothesis of initial uniform volume fraction)

\[ x_0 \propto \left( \frac{t}{\phi^*} \right)^{2/3} \simeq \phi_0^{1/2} t^{2/3} \]

\[ F_p \propto \sqrt{x_0} \]
\[ F_p \propto V_{\text{deposit}}^{1/4} \]

Hypothesis of steady-state concentration?
\[ V_{\text{deposit}} \propto \phi_0 t \quad \rightarrow \quad F_p \propto V_{\text{deposit}}^{1/3} \]
Advancing VS receding contact lines

- Comparison between advancing and receding contact lines …
  (same suspensions, similar evaporation rates)
- **The stick-slip is much stronger for advancing contact lines !!!!**
  For a given pinning time, the contact angle variation is about 10 times higher for advancing CL
- The scalings *seem* to be different.
  - Advancing: \( F_p \propto t^{1/2} \)
  - Receding: \( F_p \propto t^{1/3} \)
- The transition mechanism from stick-slip to steady velocity is different:
  - Advancing: intermittent pinning events
  - Receding: pinning decrease to ‘zero’ … (1 or 2 particle layers)

In both cases, \( F_p \) grows at short times faster than \( F_{CL} \)

Necessary condition for stick-slip
3. Stick-slip phenomena

- Advancing contact lines of colloidal suspension
- Receding contact lines of colloidal suspension
- Polymer solutions
Polymer solutions

Receding contact lines .... => **NO PINNING !!!**

**Colloidal suspension**

$V = 0.8 \text{um/s, 3 wt. \%,}$

$v_{ev} = 0.42 \mu\text{m/s}$

But similar stick-slip behavior at higher evaporation rates

**Advancing contact lines .... => NO PINNING !!!**

But **contact angle variations.**

**Polyacrylamide in water**

$V = 0.5 \text{um/s, 5 wt. \%,}$

$v_{ev} = 0.28 \mu\text{m/s}$

**Polymer solution**

Monteux et al., EPL 2008
Depinning of polymer solutions

**Kajiyama, *Langmuir* 2009**

Depinning does not depend on the substrate

... but depends on the system (polymer+solvant)

*Below a given contact angle, the CL recedes*

No “slip” after the depinning...
Depinning of polymer solutions


System properties

Marganoni?

Viscosity?
Moving CL of evaporative polymer solutions

Large Ca : standard Cox-Voinov law

\[ \theta^3 - \theta_0^3 = 9 \frac{\eta V}{\gamma} \log \left( \frac{L}{a} \right) \]

Low Ca : Increase of the viscosity in the CL region \( \Rightarrow \) contact angle variations but no pinning

\[ \Phi(x) = \Phi_\infty \left( 1 + \frac{8J_0}{V_{adv} \theta x^{1/2}} \right) \]

model for \( \phi_{eff}(V) \)

steady state volume fraction due to evaporation

model for \( \eta(\phi) \)

Semi-dilute polymers in \( \theta \)-solvant:

\[ \eta(\phi) \simeq \eta_0 \left( \frac{\phi}{\phi_\infty} \right)^n, \quad n = 2 \]

Integration leads to

\[ \theta^5 - \theta_{eq}^5 \propto \frac{\eta_0 V_{adv}^{-1} J_0^2}{\gamma a} \]
Polymer solutions

Validation:

• effect of evaporation rate => ok
• polymer size … ?

It is the viscosity VS volume fraction relationship that seems to be important …

Monteux et al., EPL 2008
Conclusions

- Steady state deposit thickness:

- Pinning: geometry of the deposit and effective contact angle

- Pinning VS depinning:
  - Competition between contact line stiffness and growing of the deposit
  - The pinning force due to the deposit is a (empiric) function of the deposit volume => quasi-static pinning
  - Polymer solutions: the rheology is important

Open questions:
- Effective contact angle on a wet porous substrate
- Difference between advancing and receding
- Influence of system properties … rheology!
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