Self-Assembly and Percolation in Colloidal Droplet Evaporation

Ching-Ling Hsu (許經菱)

Department of Physics, CYCU

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Self-Assembly

Metal nanoparticles

Planar array of 1D chains

2D superlattice

3D superlattice

T. Teranishi, C. R. Chimie 6 (2003) 979
Colloidal Droplet Evaporation
Capillary flow as the cause of ring stains from dried liquid drops

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

* James Franck Institute, 5640 South Ellis Avenue, Chicago, Illinois 60637, USA
† Department of Computer Science, University of Chicago, 1100 East 58th Street, Chicago, Illinois 60637, USA

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 they influence processes such as printing, washing and coating1–3. Ring deposits also provide a potential means to write or deposit a fine pattern onto a surface. Here we ascribe the characteristic pattern of the deposition to a form of capillary flow in which pinning of the contact line of the drying drop ensures that liquid evaporating from the edge is replenished by liquid from the interior. The resulting outward flow can carry virtually all the dispersed material to the edge. This mechanism

Figure 1 A ring stain and a demonstration of the physical processes involved in production of such a stain. a, A 2-cm-diameter drop of coffee containing 1 wt% solids has dried to form a perimeter ring, accentuated in regions of high curvature. b, Spheres in water during evaporation, as described in the text. Multiple exposures are superimposed to indicate the motion of the microspheres.
Coffee Rings (Capillary Flow)

The contact line is pinned.

The Early Stage

1 μm PS (polystyrene) + water
The Middle Stage

1 μm PS (polystyrene) + water
The Final Stage

1 μm PS (polystyrene) + water
Patterns from Colloidal Droplet Evaporation


Fig. 4. Bright-field TEM micrographs of monolayer films of 3.7-nm gold clusters supported on a thin flake of MoS$_2$. (A) Unlinked array encapsulated by dodecanethiol. (B) Cluster network linked by 20 ADT.
Patterns from Colloidal Droplet Evaporation

Patterns from Colloidal Droplet Evaporation


Patterns from Colloidal Droplet Evaporation

FIG. 9. Deposit left by drops of 1-μm microspheres dried on mica. The initial volume fractions reading from left to right and from top to bottom are 2.0%, 1.0%, 0.5%, 0.25%, 0.13%, and 0.063%. The diameter of each drop is approximately 6 mm.

FIG. 17. Deposit left by 0.1-μm microspheres of 0.5% initial volume fraction when a SDS surfactant is added. The center of the drop lies below the image so that the contact line moved from top to bottom. In each image the scale bar corresponds to 50 μm. In frames (a)–(d) the concentration of surfactant is $8.1 \times 10^{-4} M$, $4.3 \times 10^{-4} M$, $1.4 \times 10^{-4} M$, and $4.8 \times 10^{-5} M$, respectively.

Velocity of Capillary Flow

\[ v(r,t) = -\frac{1}{\rho rh} \int_0^r dr \ r \left( J_s(r,t) \sqrt{1 + \left( \frac{\partial h}{\partial r} \right)^2 + \rho \frac{\partial h}{\partial t}} \right) \]


\[ v = 10^{-5} \sim 10^{-6} \text{ m/s} \quad \text{(near the ring)} \]
Factors in Colloidal Droplet Evaporation

- pinning sites ↔ substrate surface
- evaporation rate ↔ capillary flow
- particle concentration
- particle-particle interaction
- and ?
Patterns from Colloidal Droplet Evaporation

Patterns from Colloidal Droplet Evaporation

150 nm PS

5% 25%

95% >100%
A Lattice-gas Model

\[ H = -\varepsilon_n \sum_{ij} n_i n_j - \varepsilon_l \sum_{ij} l_i l_j - \varepsilon_{nl} \sum_{ij} n_i l_j - \mu \sum_i l_i \]

Nanoparticle: \( n_i = 1 \) and \( l_i = 0 \)
Liquid: \( n_i = 0 \) and \( l_i = 1 \)
Vapor: \( n_i = 0 \) and \( l_i = 0 \)

- \( \Box_n \): nanoparticle-nanoparticle interaction energy
- \( \Box_l \): liquid-liquid interaction energy
- \( \Box_{nl} \): nanoparticle-liquid interaction
- \( \lambda \): chemical potential for the solvent evaporation.

The nanoparticles can only diffuse into the cells filled with liquid.
\[ H = -\varepsilon_n \sum_{\langle ij \rangle} n_i n_j - \varepsilon_l \sum_{\langle ij \rangle} l_i l_j - \varepsilon_{nl} \sum_{\langle ij \rangle} n_i l_j - \mu \sum_i l_i \]

\[ \varepsilon_n = 1.0kT, \varepsilon_l = 4.0kT, \varepsilon_{nl} = 3.0kT, \mu = -4.5kT \]
150nm PS (polystyrene) + methanol

\[ \varepsilon_n = -1.0kT, \varepsilon_l = -1.0kT, \varepsilon_{nl} = 1.0kT \]
150nm PS + methanol

150nm PS + water

a

b

30%
The Hildebrand solubility parameter $\sigma$ (square root of cohesive energy density) of water and methanol are 23.4 and 14.5 (cal/cm$^3$)$^{1/2}$.

Methanol is a nonelectrolyte. The interparticle repulsion is larger in methanol.

$2 \sigma_{nl} > \sigma_l + \sigma_n$

$2 \sigma_{nl} - (\sigma_l + \sigma_n)$ needs to be positive to keep the colloid from aggregation.

PS surfaces are hydrophobic generally.
\[ \varepsilon_n = -1.0kT, \varepsilon_i = 1.0kT, \varepsilon_{nl} = 1.0kT \]

\[ \varepsilon_n = -0.1kT, \varepsilon_i = 2.0kT, \varepsilon_{nl} = 2.0kT \]
Colloidal Droplet Evaporation

Au nanoparticle + dithiol
I-V characteristic curves
Fig. 4. Bright-field TEM micrographs of monolayer films of 3.7-nm gold clusters supported on a thin flake of MoS$_2$. (A) Unlinked array encapsulated by dodecanethiol. (B) Cluster network linked by 20 ADT.
Conductive Nanoparticles

charging energy \[ E = \frac{e^2}{2C} \]


http://www.sp.phy.cam.ac.uk/SPWeb/research/CB.html
Coulomb Blockade

Single Electron Transistor (SET)

Ordered 2D Nanoparticle Films

\[ r \approx 3.7 \text{ nm} \]

\[ C = 4\pi\varepsilon\varepsilon_0 r \approx 7 \times 10^{-28} \text{ F} \quad E = \frac{e^2}{2C} \approx 108 \text{ meV} \]

\[ G = G_\infty e^{-E_A/k_B T} \]

\[ R_D \approx G_\infty^{-1} = 0.9 \text{ M\Omega} \]

\[ E_A = 97 \text{ meV} \]

Disordered 2D ~ 3D

Percolation
Quasi-1D path

22nm Au  22nm Au  4.2nm Au

5nm Au nanoparticles

\[ C = 4\pi\varepsilon\varepsilon_0 r \approx 1 \times 10^{-27} \text{ F} \quad E = \frac{e^2}{2C} \approx 80 \text{ meV} \]

\[ G = G_\infty e^{-E_A/k_B T} \quad R_D \approx G_\infty^{-1} = 3.5 \text{ M\Omega} \quad E_A = 18 \text{ meV} \]
$$V_{1/2} \sim 5.44 \frac{NkT}{e},$$

$$\Delta G/G_t \sim (1/6)[2(N-1)/N][e^2/2C]/kT,$$

$N$: the number of junctions.
$V_{1/2}$: the width at half-minimum of the normalized differential conductance suppression; $\Delta G/G_t$ is its depth.
$C$: the capacitance of a single junction.

5nm Au nanoparticles

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5nm Au nanoparticles + 1,6-hexanedithiol

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\[ C = 4\pi\varepsilon\varepsilon_0 r \approx 1 \times 10^{-27} F \]
\[ E = \frac{e^2}{2C} \approx 80\text{meV} \]
Percolated Network
Table I. Selected percolation thresholds for various lattices. 'Site' refers to site percolation and 'bond' to bond percolation. In all cases, only nearest neighbours form clusters, and no correlations are allowed between different sites or bonds. If the result is not exact (see text), the error probably affects only the last decimal.

<table>
<thead>
<tr>
<th>Lattice</th>
<th>Site</th>
<th>Bond</th>
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<tbody>
<tr>
<td>Honeycomb</td>
<td>0.6962</td>
<td>0.65271</td>
</tr>
<tr>
<td>Square</td>
<td><strong>0.592746</strong></td>
<td>0.50000</td>
</tr>
<tr>
<td>Triangular</td>
<td>0.50000</td>
<td>0.34729</td>
</tr>
<tr>
<td>Diamond</td>
<td>0.43</td>
<td>0.388</td>
</tr>
<tr>
<td>Simple cubic</td>
<td>0.3116</td>
<td>0.2488</td>
</tr>
<tr>
<td>BCC</td>
<td>0.246</td>
<td>0.1803</td>
</tr>
<tr>
<td>FCC</td>
<td>0.198</td>
<td>0.119</td>
</tr>
<tr>
<td>d = 4 hypercubic</td>
<td>0.197</td>
<td>0.1601</td>
</tr>
<tr>
<td>d = 5 hypercubic</td>
<td>0.141</td>
<td>0.1182</td>
</tr>
<tr>
<td>d = 6 hypercubic</td>
<td>0.107</td>
<td>0.0942</td>
</tr>
<tr>
<td>d = 7 hypercubic</td>
<td>0.089</td>
<td>0.0787</td>
</tr>
</tbody>
</table>
$\varepsilon_n = 2.0kT, \varepsilon_l = 1.0kT, \varepsilon_{nl} = 1.5kT, \mu = -2.25kT$
The two-dimensional lattice gas model can simulate the nanoparticle aggregation patterns during solvent evaporation with Monte Carlo dynamics. The percolation threshold is affected by self-assembly. It is possible to be less than the classical value. The electrical transport of the nanoparticle film near the percolation threshold may be through a quasi-1D percolated path.
3D model?

Controlling Pattern Formation in Nanoparticle Assemblies via Directed Solvent Dewetting

Christopher P. Martin, Matthew O. Blunt, Emmanuelle Pauliac-Vaujour, Andrew Stannard, and Philip Moriarty

School of Physics and Astronomy, The University of Nottingham, University Park, Nottingham NG7 2RD, United Kingdom

Ioan Vancea and Uwe Thiele

Max-Planck-Institut für Physik komplexer Systeme, Nöthnitzer Strasse 38, D-01187 Dresden, Germany
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We have achieved highly localized control of pattern formation in two-dimensional nanoparticle assemblies by direct modification of solvent dewetting dynamics. A striking dependence of nanoparticle organization on the size of atomic force microscope-generated surface heterogeneities is observed and reproduced in numerical simulations. Nanoscale features induce a rupture of the solvent-nanoparticle film, causing the local flow of solvent to carry nanoparticles into confinement. Microscale heterogeneities instead slow the evaporation of the solvent, producing a remarkably abrupt interface between different nanoparticle patterns.

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Colloidal solutions of nanoparticles are simple to synthesize, exceptionally stable, and can be made from materials with a wide variety of chemical and electrical properties. Their versatility makes them ideal building blocks for the next generation of nanoscale electronic devices. When deposited on a surface, colloidal nanoparticles form a diverse array of patterns [1–8] for which the behavior of the solvent plays a key role. Isolated islands, wormlike domains, continuous labyrinthine patterns, and polygonal networks can each be produced by varying the experimental conditions [1,5,9,10]. Although there have been impressive recent examples of the exploitation of intermittent contact mode with closed-loop control was used for both imaging and local oxidation of the H:Si(111) samples. Oxidation was carried out using PtIr-coated silicon probes at a bias of −10 V and in 70% humidity. Octanethiol-passivated Au nanoparticles of ∼2 nm core diameter (±8%) were prepared in toluene [17]. For experiments involving rapid solvent evaporation, a 25 μl droplet of an appropriately diluted solution (typical concentration values ranged from 0.1 mg/ml to 1 mg/ml) was placed on the locally oxidized substrate and the sample subsequently spun at 4 k rpm. Slow evaporation was induced by keeping the solvent in a meniscus on the sample by means of a
FIG. 2 (color online). (a) An AFM image of gold nanoparticles spun from toluene onto H:Si(111) with an AFM-patterned 4 \( \mu \text{m} \times 4 \mu \text{m} \) square of oxide in the center and (b) the result of a simulation with \( |\mu| \) 6\% lower on the oxide area.

FIG. 3 (color online). (a) An AFM image showing the effect of 1 \( \mu \text{m} \) diameter rings of oxide on nanoparticle pattern formation. The oxide features in the image are almost entirely free of Au nanoparticles and a denuded zone extends round each ring for a further 100 nm. In the regions between the rings, the Au nanoparticle layer forms a network arising from nucleated dewetting of the solvent. (b) A simulation in which sections of solvent and particles have been removed (indicated in white) to approximate the effect of dewetting from the oxide regions before the realm of the simulation.