ELECTRIC FIELD-DIRECTED PATTERNING OF MOLECULES ON A SOLID SURFACE

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Abstract: Adsorbed on a solid surface, a molecule can migrate and carry an electric dipole moment. A nonuniform electric field can direct the motion of the molecule. A collection of the same molecules may aggregate into a monolayer island on the solid surface. Place such molecules on a dielectric substrate surface, beneath which an array of electrodes is buried. By varying the voltages of the electrodes individually, it is possible to program molecular patterning, direct an island to move in a desired trajectory, or merge several islands into a larger one. This article develops a phase field model to simulate the molecular motion and patterning under the combined actions of dipole moments, intermolecular forces, entropy, and electrodes.

Key words: self-assembly, diffusion, adsorbate, electric dipole

1.   INTRODUCTION

When a molecule from liquid or vacuum attaches to a solid surface, the total energy of the system reduces by an amount. Provided the energy reduction is much larger than the thermal fluctuation, the molecule will stay adsorbed on the surface. In the absent of external interference, the molecule adsorbed performs a random walk. Such motion is thermally activated, its rate depending on the ratio of the migration barrier energy to the thermal energy [1].

Most asymmetric molecules intrinsically carry electric dipole moments. Even if the molecule is symmetric and nonpolar when isolated, the adsorption breaks the symmetry. The resulting asymmetric in charge distribution gives rise to a dipole moment. It is also possible to increase the

dipole moment greatly by implanting a specific functional group [**2**]. The competition between the dipole-dipole repulsion and the intermolecular attraction aggregates the adsorbates into islands or stripes [**3**]. As the solid surface is isotropic, the pattern formed is randomly distributed and lack of long range order. Surface curvature could help to form better arranged pattern [**4**], but it's still far from the non-periodic pattern needed for micro-fabrication.

The motion of the adsorbates can be directed by a non-uniform electric field. Such motion has been demonstrated experimentally for cesium atoms on a doped GaAs substrate [**5**]. Other experiments of electric field directed motion are adatoms on metal surfaces [**6**] and lipids on air/water interface [**7**]. The scanning tunneling microscope tip servers as a strong tool in searching for better adsorbate-substrate pairs and studying the migration processes, but the lack of parallel ability and versatility limits its practical usage. A mask with topographic profile could guide a more complex pattern [**8**], but the pattern could never be changed once formed, and the alignment of the mask within a small distance to the substrate has technical difficulties. An array of electrodes, on which voltage could be set individually, forms a perfect candidate for the guide of the molecular assembly.

Fig. 1 shows the design. This design requires electrodes in nano-scale. Integrated circuits today contain feature size below 100 nm. Methods to fabricate complex structures of nanometer sizes are under intensive development. This article assumes that the technique for nano-scale electrode array will be available, simulates the use of such electrodes to guide the molecular motion, and discusses the potential of reconfigurable patterns and molecular cars.
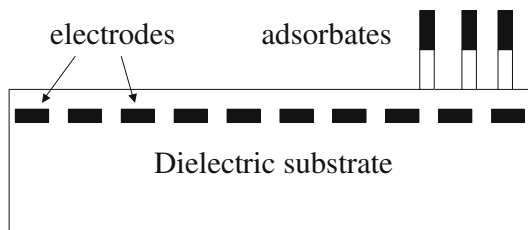
Figure 1. A dielectric substrate, with adsorbates migrating on its surface, and electrodes buried beneath the surface. The adsorbates carry electric dipole moments. Vary the voltage of the electrodes individually, one can program the motion and assembly of the adsorbates.

2.   MODELING

The space above the substrate can be vacuum or a dielectric fluid. We will refer to the top space as fluid, and the dielectric substrate as solid. Let (x_1, x_2, x_3) be the spatial coordinates, and the plane $(x_3 = 0)$ be the solid surface on which molecules are adsorbed. Let C be the adsorbate coverage, restricted in the interval $0 < C < 1$. Represent the adsorbate distribution by the time-dependent field $C(x_1, x_2, t)$. During the time of interest, we assume that the solid surface no longer exchange molecules with the environment, so that the average coverage, C_0, is invariant.

The adsorbates may form a single phase or separate into two phases, depending on the magnitude of the inter-adsorbate attraction relative to the thermal energy. We describe the binary mixture of the occupied and the vacant surface sites as a regular solution. The free energy of mixing per unit surface area is

$$g(C) = \Lambda k_B T \left[C \ln C + (1 - C) \ln(1 - C) + \Omega C(1 - C) \right], \tag{1}$$

where Λ is the number of surface sites per unit area, k_B Boltzmann's constant, T the absolute temperature, and Ω the dimensionless parameter that measures the interadsorbate attraction relative to the thermal energy. The first two terms in the bracket come from the entropy of mixing, and the third term from the enthalpy of mixing. When $\Omega < 2$, the thermal energy prevails, the function $g(C)$ has a single well, and the binary mixture forms a solution. When $\Omega > 2$, the inter-adsorbate attraction prevails, the function $g(C)$ has double wells, and the binary mixture separates into two phases. While the regular solution model is one of many that can be invoked, it does have the ingredients essential to the phenomenon.

To incorporate the dipole-dipole and dipole-electrode interactions, we need to solve the electric field in both the fluid and the solid. The adsorbate mobility is low compared to the charge mobility in the electrodes. At a certain time, given a distribution of the adsorbates, the electric field is governed by electrostatic equations. Let $\Psi(x_1, x_2, x_3, t)$ be the electric potential field. Assuming that no excess charge exists inside the dielectric fluid and solid, Ψ obeys the Laplace equation. The electrode array underneath the dielectric, at a depth H, forms a boundary condition. A pre-programmed electric potential field is applied:

$$\Psi(x_1, x_2, -H, t) = Us(x_1, x_2, t), \tag{2}$$

where U represents the voltage magnitude, and s the time-dependent electrode voltage pattern, taking to be a spatially continuous function.

The electric dipoles of the adsorbates cause a change in the surface potential, which can be measured experimentally using the Kelvin method [7]. We assume that the surface potential is linear in the adsorbate coverage. That is, at the fluid/solid interface, $x_3 = 0$, there's a potential jump:

$$\Psi\left(x_1, x_2, 0^+, t\right) - \Psi\left(x_1, x_2, 0^-, t\right) = \zeta C\left(x_1, x_2, t\right). \tag{3}$$

The slope ζ is a material constant. This boundary condition couples the electrostatic field to the adsorbate distribution. Assuming the adsorbates to be electrically neutral, the electric displacement component normal to the interface, D_3, is continuous across the interface:

$$-\varepsilon_f \left.\frac{\partial \Psi}{\partial x_3}\right|_{x_3=0^+} = -\varepsilon_s \left.\frac{\partial \Psi}{\partial x_3}\right|_{x_3=0^-} = D_3 , \tag{4}$$

where ε_f and ε_s are the permittivity of the fluid and the solid. The Laplace equation, together with the boundary conditions, determines the electric potential field.

The driving force on an adsorbate, **f**, is the reduction of the free energy of the system associated with the adsorbate moving a unit distance. Following the procedure in [8], we obtain that

$$\mathbf{f} = -\frac{1}{\Lambda}\nabla\left(\frac{\partial g}{\partial C} - 2h\nabla^2 C - \zeta D_3\right). \tag{5}$$

The first term comes from the free energy of mixing, which accounts for the thermal energy and the inter-adsorbate interaction. The second term represents the Cahn-Hilliard gradient energy [10], where h is a constant. The third term accounts for the dipole-dipole and dipole-electrode interactions. Assume that the adsorbate flux is linearly proportional to the driving force, $\mathbf{J} = M\mathbf{f}$, where M is the adsorbate mobility. The conservation of the adsorbates requires that $\Lambda \partial C / \partial t = -\nabla \cdot \mathbf{J}$. These considerations, together with Eqn. 5, lead to the diffusion equation:

$$\frac{\partial C}{\partial t} = \frac{M}{\Lambda^2}\nabla^2\left(\frac{\partial g}{\partial C} - 2h\nabla^2 C - \zeta D_3\right). \tag{6}$$

The third term in the bracket couples the evolution of the adsorbate distribution to the electrostatic field.

3. SIMULATION

A comparison between the first two terms the parenthesis of Eqn. 6 defines a length scale:

$$b = \left(\frac{h}{\Lambda k_B T}\right)^{1/2},\tag{7}$$

which scales the width of the phase boundary. To resolve events occurring over this length scale, we introduce a time scale, $\tau = b^2 / D$, where D is the diffusivity, scaling as $D \sim M k_B T / \Lambda$. Disregarding a dimensionless factor, we have the time scale

$$\tau = \frac{h}{M(k_B T)^2}.\tag{8}$$

In calculation, we normalize the spatial coordinates by b and time by τ. A dimensionless number, representing the relative magnitude of the dipole moment to the intermolecular attraction, appears in the normalized equation:

$$W = \frac{\varepsilon_f \zeta^2}{\sqrt{h\Lambda k_B T}}.\tag{9}$$

W determines the equilibrium island size.

To evolve Eqn. 6, one needs to solve the electrostatic boundary value problem in every time step. Fortunately in the current system, the boundary value problem could be solved analytically in Fourier space. Take the Fourier transform of a field variable with respect to the two lateral coordinates x_1 and x_2, and let k_1 and k_2 be the corresponding coordinates in the Fourier space. The Laplace equation becomes an ordinary differential equation $d^2\hat{\Psi}/dx_3^2 = k^2\hat{\Psi}$, where $k = \sqrt{k_1^2 + k_2^2}$. The solution takes the form $\hat{\Psi} = A\exp(kx_3) + B\exp(-kx_3)$, with constants A and B determined by the boundary conditions. The solution gives the electric displacement at the fluid/solid interface:

$$\hat{D}_3 = \frac{Uk\hat{s} + \zeta\hat{C}k\cosh kH}{\dfrac{\cosh kH}{\varepsilon_f} + \dfrac{\sinh kH}{\varepsilon_s}}.\tag{10}$$

Applying the solution to the diffusion Eqn. 6, we have the evolving equation in the Fourier space:

$$\frac{\partial \hat{C}}{\partial t} = -k^2 \hat{P} - 2k^4 \hat{C} + Wk^3 \frac{(U/\zeta)\hat{s} + \cosh kH \hat{C}}{\cosh kH + \varepsilon_f/\varepsilon_s \sinh kH}. \tag{11}$$

Here both k and H are normalized by b, and $\hat{P}(k_1, k_2)$ is the Fourier transform of the function

$$P(x_1, x_2) = \ln\left(\frac{C}{1-C}\right) + \Omega(1 - 2C). \tag{12}$$

A commonly used numerical scheme is adopted here. The computational cell is divided into 256×256 grids, and subject to a periodical boundary condition at all edges. We evolve the values of the C-field at all the grid points. At a given time, the C-values are known in both the real and the Fourier spaces. Calculate the nonlinear function P at all the grid points in the real space according to Eqn. 12, and transform them into the Fourier space. Update $\hat{C}$ at all grid points in the Fourier space according to Eqn. 11, and perform the inverse Fourier transform to obtain C-values in the real space. Repeat this procedure for many time steps. The results are plotted as a gray scale contour of C-values in the real space.

4.   RESULTS

The model has many dimensionless numbers: Ω, W, $\varepsilon_f/\varepsilon_s$, H/b, U/ζ and the average coverage C_0. In addition, the initial adsorbate distribution field is spatial dependent, and the electrode voltage pattern is spatial and time dependent. A survey of the full parameter space is beyond the scope of this paper. In the following numerical examples, unless otherwise noted, we set $\Omega = 2.2$, $W = 2$, $\varepsilon_f/\varepsilon_s = 1$, $H/b = 10$. For the value $\Omega = 2.2$, the free energy of mixing, $g(C)$, has two wells at the coverage $C = 0.25$ and $C = 0.75$. To illustrate several considerations, we will vary U/ζ, the initial adsorbate distribution, and the electrode voltage pattern.

4.1   Electric field-directed assembly

When the adsorbates separate into two phases, the phase boundary energy drives the phases to coarsen. The molecular dipole moments are aligned in the same direction: they repel one another. Consequently, the

dipole-dipole interactions drive the phases to refine. In equilibrium, the phases will reach equilibrium sizes, typically ranging from nanometers to micrometers [**11-13**]. Because of the symmetry of the system, the patterns assembled don't have a long-range order. Here we use the electrode voltage pattern to direct the assembly processes.

Fig. 2 shows two time sequences, guided by different electrode voltage patterns, the top row by an array of stripes, and the bottom row by a lattice of dots. At $t = 0$, adsorbates distribute uniformly, with coverage $C_0 = 0.5$. A small magnitude of the electrode voltage, $U / \zeta = 0.02$, is prescribed. In the absence of the electrode voltage pattern, the adsorbates at the average coverage $C_0 = 0.5$ self-assemble into a pattern of randomly oriented noodles (e.g., **11**). As illustrated in Fig. 2, the small-magnitude electrode voltage patterns can guide the adsorbates to form straight stripes and other patterns.
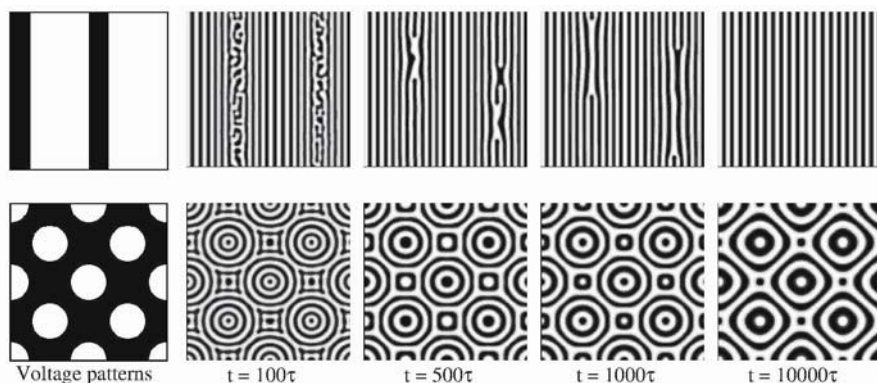

Figure 2. Electric field-guided self-assembly. In the top row, the electrode voltage pattern is an array of widely spaced stripes, and the adsorbates assemble into an array of finely spaced stripes. In the bottom row, the electrode voltage pattern is an array of large dots, which guide the assembly of the adsorbate pattern. In both cases, the electrode voltage is small, so that adsorbates still retain the natural pattern of fine stripes, and the electrode voltage only affects the overall layout.

One can change the electrode voltage pattern at any time, so that the adsorbate pattern is reconfigurable. Fig. 3 shows a time sequence. The initial adsorbate distribution is uniform, with coverage $C_0 = 0.35$. Prescribe the electrode array with a voltage pattern of the letter P using a relative high voltage, $U / \zeta = 1$. Under the guidance of the electrode voltage pattern, the adsorbates form a pattern of the letter P. In the background, the remaining adsorbates self-assemble into islands. We then change the electrode voltage pattern into the letter H. The adsorbates reassemble to form the letter H. The newly assembled pattern bears no resemblance to the old one.

Figure 3. Reconfigurable assembly. Initially, the electrode voltage pattern is the letter P, and the adsorbates assemble accordingly. Then switch the electrode voltage pattern to the letter H, and the adsorbates re-assemble. The electrode voltage is high, so that the electrode voltage pattern overwhelms the natural pattern of the adsorbates.

The above examples demonstrate that a static electrode voltage pattern can either guide the self-assembly of the adsorbates, or impose a desired pattern. The main difference in the two operations is the relative magnitude of the electrode voltage to the surface potential, U / ζ. A small-amplitude electrode voltage pattern guides the overall layout of the stripes. The natural pattern such as the stripes is more or less preserved. A large-amplitude electrode voltage pattern overwhelms the natural pattern, and the adsorbate pattern is nearly a replica of the electrode voltage pattern.

4.2   Programmable motion

When the electrode voltage pattern is time-dependent, the adsorbates will move around. For example, consider a single island of aggregated adsorbates. If one applies voltage on the electrodes sequentially, the island can be propelled to move in a desired direction. Fig. 4 shows two time sequences, using parameters $U / \zeta = 1$, $C_0 = 0.2$. At such a low coverage, no phase separation takes place in the absence of the external electric field. We apply a circular shaped voltage pattern at the center to assemble the adsorbates. Subsequently, we program the electrode voltage pattern into a traveling wave. Fig. 4 shows snap shots for islands driven at two electrode voltage wave velocities. When the voltage wave moves slowly ($v = 0.02b/\tau$), the island distorts somewhat, but follows the motion. When the voltage wave moves too fast ($v = 0.05b/\tau$), the island ruptures.

Fig. 5 shows that the electrode voltage can be programmed to split an island. The parameters used are the same as those for Fig. 4. Again, we apply a circular shaped voltage pattern at the center. After a time of 2000τ, an island of the size similar to the electrode voltage pattern assembles. We then divide the voltage pattern into two halves, and move them apart with a constant velocity of $v = 0.025b/\tau$. The island also splits into two halves, which follow the two electrode voltage waves. By reversing the process, we could also combine two islands into one.
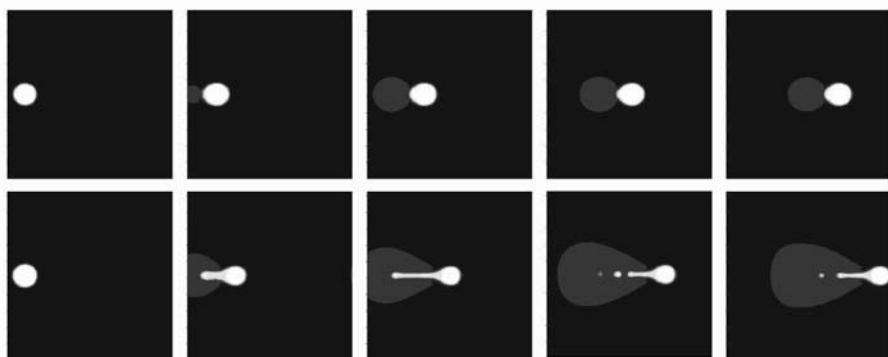
Figure 4. Top row: an adsorbate island driven by a slow electrode voltage wave at a low velocity. Bottom row: an adsorbate island driven by a fast electrode voltage wave.
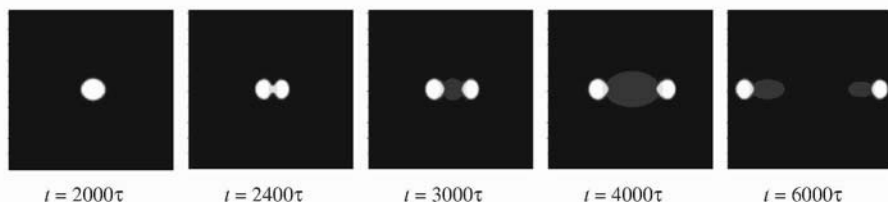

Figure 5. Splitting an island. The initial electrode voltage pattern is a single circular dot. The voltage pattern is then divided into two halves, and move in the opposite directions. The adsorbate island is split into two smaller islands.

5.   CONCLUSION

Adsorbed on a solid surface, a molecule carries an electric dipole moment, and moves on the surface by a thermally-activated process. A patterned electrode array can direct the motion of the molecules. When a collection of the molecule partially covers the solid surface, their motion is influenced by the entropy, the intermolecular attraction, the dipole-dipole interaction, as well as the dipole-electrode interaction. We develop a phase field model to evolve adsorbate distribution field under the multiple thermodynamic forces. An array of electrodes can be programmed to guide the assembly of the adsorbates, or move the adsorbates in desired ways. Our numerical simulation illustrates the potential of the reconfigurable assembly and the programmable adsorbate motion. Technological implications of this model are explored in [**14**].

ACKNOWLEDGMENTS

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