C. Isenberg, *The Science of Soap Films and Soap Bubbles*, New Y
Dover, 1992.

The beautifully illustrated book by Hildebrandt and Tromba recou
much of the history of the study of minimal and capillary surfaces.

S. Hildebrandt and A. Tromba, *The Parsimonious Universe: Shape
Form in the Natural World*, New York: Springer-Verlag, 1996.

6.9 Notes

1. The catenary is, of course, the shape assumed by a chain hanging i
gravitational field.

2. The reader should consult the works of H. Wente, R. Finn, and S. Hi
brandt for a complete analysis of symmetry breaking in capillary surfaces.
mathematical analysis of such problems often becomes subtle and difficul

3. This type of surface is also called a liquid bridge.

Chapter 7

Dynamic Self-Assembly

Science moves, but slowly, slowly, creeping on from point to point.

Tennyson, *Locksley Hall*

7.1 Introduction

In Chapter 1 we examined the reasons why there is so much interest in self-assembly today. We offered a quote from Richard P. Feynman that captured one reason for much of the excitement:

> The biological example of writing information on a small scale has inspired me to think of something that should be possible. Biology is not simply writing information; it is *doing something* about it. A biological system can be exceedingly small. Many of the cells are very tiny, but they are very active; they manufacture various substances; they walk around; they wiggle; and they do all kinds of marvellous things – all on a very small scale. Also, they store information. Consider the possibility that we too can make a thing very small which does what we want – that we can manufacture an object that maneuvers at that level!

In the last six chapters we've strayed a bit from Feynman's vision. None of the systems that we've described thus far are terribly active. They don't manufacture, they don't walk around, they don't wiggle; they might be marvellous in their own right, but, they aren't very active. As we saw in the last chapter, most of the systems we've been studying are examples of *static* self-assembling systems. In this chapter we turn our attention to systems that do walk around, do wiggle, and do maneuver. We examine *dynamic* self-assembling systems.

In Chapter 1, we defined dynamic self-assembly. We categorized dynamic self-assembling systems as a subclass of self-assembling systems that leads to stable non-equilibrium structures. We said that these structures remained ordered only so long as the system continued to dissipate energy. The inspiration for studying such systems is precisely that identified by Feynman – biology.

Although the biological examples we studied in Chapter 3 were largely sta
it does not take much imagination to see that most of biology is dynamic a
must rely upon some form of dynamic self-assembly. If only we could learn
do what nature does so easily, build cells, with all the concomitant proper
that implies, we'd have achieved the ultimate goal in self-assembly resear

Sadly, we're not yet close. Research in dynamic self-assembly is truly
its infancy. Yet, some progress has been made, and that is the subject
this chapter. Here, we'll examine what has been done, attempt to underst
dynamic self-assembly from the perspective of Chapter 4, and attempt
understand the sorts of unique design problem that arise in this area.

We begin in Section 7.2 with a detailed look at a prototypical exampl
dynamic self-assembly. Our system consists of conducting particles suspen
in a dielectric fluid and placed in an electric field. As we'll see, these parti
become active and form simple ordered structures. We'll carefully look at t
system from the viewpoint of Chapter 4 and identify the role of structu
particles, binding forces, an environment, and driving forces in this syst
We'll learn that one feature of dynamic self-assembling systems is that p
ticle interaction must be competitive. At times, particles attract, at ot
times the same particles repel. In addition, this interaction can depend
externally applied environmental conditions. After discussing our simple p
totype system, we'll examine several examples of engineered systems that
conducting particles in an electric field to create nanoscale and microsc
structures. We'll see how this idea can be applied to the creation of nanosc
wires only a few tens of nanometers in diameter, but several microns in leng
We'll also see how the properties of the prototype translate into a *self-heal*
behavior of the nanoscale system. Next, we'll see how driving a system
particles using an electric field can produce complicated temporal and spa
patterns in two and three dimensions. Again, these structures appear o
while the system is dissipating energy, and they can be controlled by man
ulating the applied field. To conclude this section we'll take a brief look
electrorheological fluids. The electrorheological system is essentially the sa
as the other systems of this section, but the number of particles has b
scaled up massively. We'll see how under the action of an applied field int
esting net-like structures can appear in these fluids. We'll also see that fr
a macroscopic point of view creating and manipulating these structures c
allow us to bring about dramatic changes in the bulk behavior of the fluid

In Section 7.3 we examine magnetically driven dynamic self-assembling s
tems. At first glance, these systems strongly resemble the magnetic s
assembling systems described in Chapter 5. Here however, in addition
magnetic forces the system also relies on the presence of a repulsive hydro
namic force. In the systems of Chapter 5, magnetic forces, either attracti
or repulsive, locked the particles in place. Here, the magnetic force not on
attracts the particle towards the center of the system but sets the partic
in motion. In turn, this creates a flow in a surrounding fluid. This flow c
ates the repulsive hydrodynamic force between particles. As we'll see, t

competition between forces creates interesting dynamic structures.

In Section 7.4 we'll take a brief look at two mechanically driven dynamic self-assembling systems. The design of these experiments is very similar to the design of the electrostatic self-assembling systems of Section 7.2, but of course, there is no electrostatic force. Nonetheless, these systems do produce complex spatial and temporal structures in two and three dimensions. The first of these two systems accomplishes this via the use of hydrodynamic forces that are both attractive and repulsive. The second of these systems is not yet understood. However, experimentalists have been able to map out a phase space for this system that shown a rich and unexpected set of behaviors.

In Section 7.5 we look at one system that accomplishes dynamic self-assembly without the use of an externally applied field. In this system, particles interact with their environment to produce a driving force. The particles are capable of binding to one another and do so as they swim about the surface of a fluid. Once bound, they continue moving, creating larger, mobile, structured complexes.

In the final section of this chapter, Section 7.6, we ask the question - What if our particles were smart? That is, if instead of merely reacting to their environment and to the presence of other particles, we imagine what might be possible if our particles could make decisions for themselves. We explain how smart particles would allow us to more successfully attack problems like the yield problem of self-assembly. We see that for a particle to be considered truly intelligent, it must be able to sense its state, communicate with its neighbors, and act on this information. We conclude with a look at a dynamic self-assembling system that uses smart particles to carry out programmable self-assembly.

7.2 A Prototype for Dynamic Self-Assembly

Take an ordinary rubber balloon, rub it on your head,[1] and you'll find it sticks to ceilings and walls. Unless your head is covered with glue, the force that allows the balloon to stick is the *Coulomb force* or more simply the *electrostatic force*. If you rub two balloons on your head, charging them in the same way, and then attempt to bring them together you'll find that they repel one another. The electrostatic force can be attractive or repulsive.

It is the combination of these attractive and repulsive properties of the electrostatic force that allows our prototypical dynamic self-assembling system to function and create ordered structures. The basic setup of the system we'll consider is shown in Figure 7.1. The system[2] consists of a small plastic tray about 15cm long, 10cm wide, and 2.5cm deep that is partially filled with a dielectric fluid. The dielectric constant of the fluid[3] used in the experiments

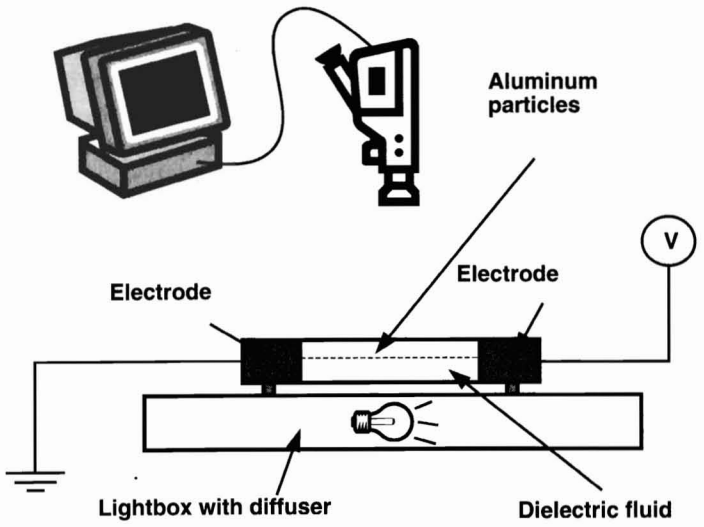

FIGURE 7.1: The experimental setup for our prototypical example of namic self-assembly.

described here was approximately 2.6. The fluid covers the tray to a de of about 1cm. The tray also holds a pair of large aluminum blocks that se as electrodes. Suspended in the fluid are several small, thin, aluminum di punched from a sheet of foil. The electrodes are attached to a regulated h voltage power supply capable of producing a potential difference of up 100kV across the electrodes. The tray sits on top of a photographic light b This enhances the contrast for the video camera positioned above the syste The video camera is attached to a video monitor allowing for easy observati during the experiments.

So, we have the basic ingredients, but what does this system do? Well, i typical experiment the aluminum particles are scattered randomly in the fl and then the voltage is turned on. At the outset, the particles are distribut like those in Figure 7.2 at time $t = 0$ or in Figure 7.3 again at time $t = 0$. On the voltage is applied, small charge imbalances on the particles cause th to drift towards one of the electrodes. Some particles will contain a slig negative charge, others will contain a slight positive charge. The partic will migrate towards the electrode that contains the opposite charge. No when a particle reaches an electrode it gives up its charge to that electro and acquires the *same* charge as the electrode. But this means that t particle will be now be repelled from that electrode. Such a particle accelerat *away* from the electrode it was previously attracted towards and moves make contact with the opposite electrode. When it reaches that electrode t process repeats. If we placed but a single particle in the fluid we'd simp

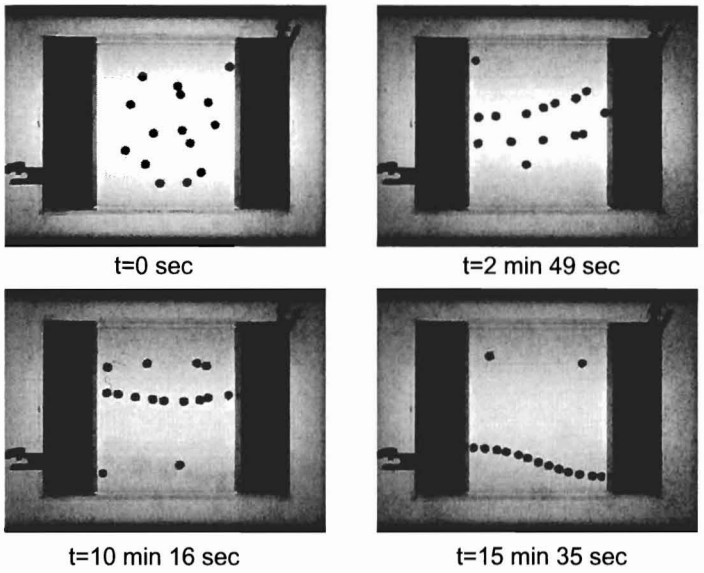

FIGURE 7.2: Frames extracted from video of our prototypical example of dynamic self-assembly. This experiment used many small particles. The applied voltage was approximately 19.8kV. Photograph by the author/MEC Lab - University of Delaware.

see it bounce back and forth between the electrodes.[4] But, there are other particles in the fluid trying to behave in the same way. As these particles pass each other, they interact. If a particle passes another particle carrying the opposite charge both particles experience an attractive force towards each other. If they encounter a particle with the same charge, they experience a repulsive force forcing them away from one another. Remarkably, over time, these repeated interactions cause the particles to self-assemble into a linear structure. This evolution can be seen in Figures 7.2 and 7.3. Notice how the vertical spread of the particles gradually narrows over time until a simple chain is formed. Particles not in the chain eventually join with little disruption to the overall dynamic behavior. In experiments the chain itself may drift, but this occurs on a timescale much longer than the timescale on which the particles oscillate within the chain.

Once the chain has formed, it persists. The system is dynamically self-assembling. If the electric field is suddenly turned off, the particles will slowly stop moving as the charge in the system is bled off, eventually returning to their initial disordered state. While in a chain each particle undergoes oscillatory motion. The particles move back and forth in a regular manner alternately colliding with and exchanging charge with their neighbors.

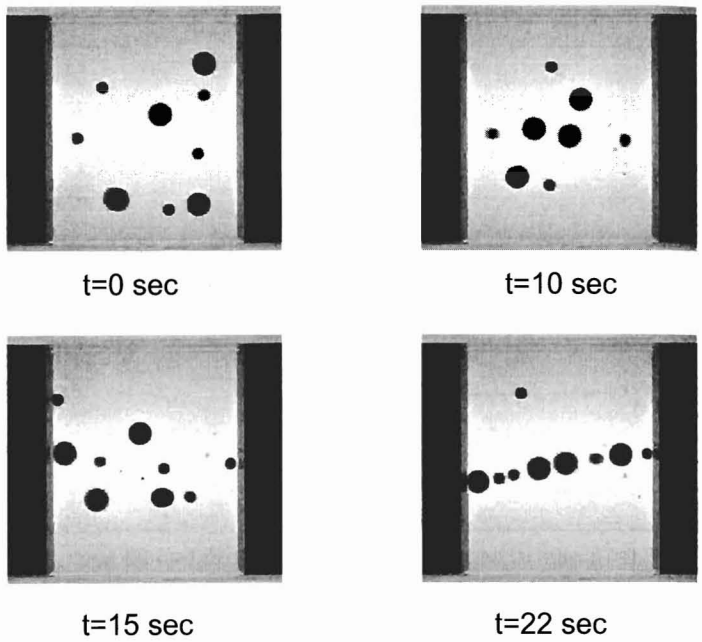

FIGURE 7.3: Frames extracted from video of our prototypical exampl dynamic self-assembly. This experiment used a mixture of large and sm particles. The applied voltage was approximately 19.8kV. Photograph by author/MEC Lab - University of Delaware.

This system may be modified in several ways. Many of these lead to ther changes in the approach to the final structure or to changes in the fi structure itself. Notice that in Figure 7.3 a mixture of particles with differ diameters is used. At the same applied voltage and same gap between electrodes, the system with the mixture forms a chain much more rapidly th the system using only small particles. From the figures we see that full ch formation took more than 15 minutes in the small particle system, but than a minute in the system with mixed particle diameters. Something apparent in the figures is that the dynamics of the particles in the assemb chain also varies between the mixed and nonmixed systems. In the syst with a uniform particle distribution, particles in the chain all oscillate w roughly the same frequency. In the system with large and small disks, small particles oscillate with a frequency much higher than the large particl Other system variables may be changed. For example, the disks may be placed by squares, rectangles, or any shape we choose. If rectangular particl are used, they are found to form a chain and in addition orient themselv along the field lines between the electrodes. If more structure is added to t

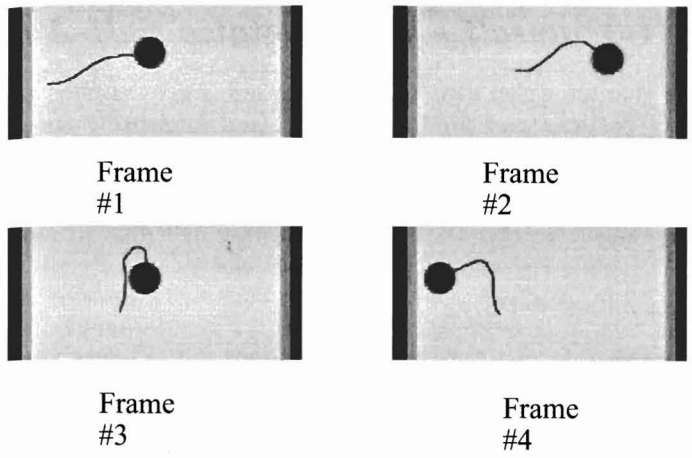

FIGURE 7.4: Frames extracted from video of the motion of a structured particle in our prototype system. Note, this particle always moves "head first." Photograph by the author/MEC Lab - University of Delaware.

particles, the changes can be even more dramatic. In Figure 7.4 we see an example of the motion of a particle consisting of an aluminum disk attached to a flexible tail. In this case, the motion of the particle is oriented. It always moves "head first," keeping the tail behind and the disk pointed towards the electrode to which it is travelling.

This simple system fits our definition of a dynamic self-assembling system. When the electric field is not present, the system remains in a state of disorder. When the field is applied the system rapidly organizes itself into a stable structure. In this state the system is dissipating energy. Some energy is lost as heat due to resistance in the electrodes and the particles while some energy is dissipated by the particles in the fluid. Yet, this system is comprised of the same four key components of self-assembling systems we identified in Chapter 4. Let's examine each of these components more closely in the context of this system and attempt to identify how this dynamic system differs from the numerous static systems we've seen.

We'll take each component in turn. In this system, the aluminum disks play the role of *structured particles*. At first glance, there is very little structure to the particles. They are simple disks. However, structure means more than simply the physical shape. As we saw in the last chapter, structure can come from a wetting pattern along particle edges or from a pattern of magnets embedded within the particle. Here, the additional structure comes from the fact that the particles are conducting. Each particle can hold a charge, so to specify the state of a particle we must give both its shape and its charge. The charge on a particle effectively represents the particles conformation.

Try It Yourself - Electrostatic Self-Assem

In this chapter we've seen how electrostatic forces applied to susp systems of particles can produce complex and interesting structures. possible to carry out some of these experiments with easily obtainab terials. The only specialized equipment you'll need is a high voltage s However, an ordinary Van de Graaff generator works fine.

Materials

- High voltage source
- Corn oil (The cheaper the brand the better it seems to work.)
- Rice
- Aluminum foil
- A clear plastic container (A container the size and shape of an ord drinking glass is perfect.)
- Wire
- Glue

Procedure Drill a small hole in the bottom of your container. Thr piece of wire through the hole and laminate a layer of foil onto the bo of the container from the *inside*. Make sure the foil makes contact wit wire. This will serve as your lower electrode. Fashion a second electrode a piece of foil and attach a wire to this electrode. This electrode will flo the surface of the corn oil. Now, partially fill your container with cor The depth will depend on the strength of your high voltage source. Start 2cm. You can add more oil if needed. Sprinkle a handful of rice grains the corn oil. Allow the rice to sink. Now, float your second electrode o of the corn oil. Attach your high voltage power supply and turn it on. should see the rice grains begin to move and form chains as in the sys described in this chapter.

Things to Try

- Let your system self-assemble a chain and then switch off the high age source. How long does it take for the chain to collapse?
- Try using very few rice grains, fewer than are needed to bridge the between your electrodes. What happens when the high voltage so is switched on?

Further Reading If you don't have access to a Van de Graaff generator, can always build a *Dirod*. The construction of this clever electrostatic erator is described in *Electrostatics: Exploring, Controlling and Using St Electricity* by A.D. Moore and J.M. Crowley.

The *binding force* in this system is the electrostatic force. Analogous to capillary systems where particles could be hydrophobic or hydrophillic, here particles can be positively charged or negatively charged. If a pair of particles is positively charged they repel, if they are both negatively charged they repel, but if they hold opposite charges, they feel an attractive force. However, unlike capillary bond systems, where the wetting properties of the particles remain fixed, here, the particles can change their type as they interact with the environment and with each other. We've already seen that contact with an electrode causes a particle to flip from one charged state to another. If particles themselves make contact this flipping can also occur. When the particles are organized into a chain they do this repeatedly, moving back and forth, making contact with their neighbors, and changing their state.

The *environment* in this system includes the fluid in which the particles are immersed, the gravitational field in which the system sits, and really the presence of the external applied electric field. We'll classify the applied electric field as a *driving force* and hold off on discussing it further for a moment. The fluid in which the particles reside exerts a drag force on the particles. Because of the scale, in this system drag forces are quite significant and inertial forces all but negligible. This means that the particles are observed to move with constant velocity rather than constant acceleration. Without the fluid, a particle leaving an electrode would accelerate continuously towards the opposite electrode. With the fluid, this acceleration is rapidly balanced by the drag force and the particles cross most of the gap with constant velocity. The gravitational field serves to orient the particles. Note that in Figures 7.2 through 7.4 every single disk is oriented with its largest side facing the camera. This is not because the particles do not have room to rotate; the particle's largest length scale is still small compared to the depth of the fluid. This is because the combination of gravity and lift forces generated on the particles as they move through the fluid keeps them oriented.

Finally, the *driving force* in this system is the applied electric field. In the absence of an applied field the particles sit in a disordered state. Perhaps, given enough time, small charge imbalance on the particles will force them to aggregate and form an ordered crystalline structure like those considered in Chapter 6. However, they will not form a chain, and will not exhibit the back and forth oscillatory motion that occurs when the field is applied. Further, the presence of the electric field and the contact with the two electrodes causes the particles to acquire a charge much larger than any they might have had initially. Further contact with the electrodes allows the particles to switch their charged states, changing their conformation.

We see that the key components of a self-assembling system identified in Chapter 4 are all present in our prototypical dynamic self-assembling system. Yet, the interaction of these components is more complex than in the static systems we've considered thus far. The major differences between this system and the static systems of previous chapters lie both in the nature of particle-particle interactions and in the interaction of particles with the environment.

Particles in this system do not remain in a single state. Rather, they
tinuously switch their states thereby continually modifying their interac
with neighboring particles. Further, the applied electric field supplies th
ergy source for this system and causes the particles to change their state.
should bear in mind that this system is constantly dissipating energy. U
static systems, when the energy supplying the driving force is removed
this system, the self-assembled structure disappears.

In designing a dynamic self-assembling structure such as this one, the
assembly researcher is still faced with the forward, backward, and yield p
lems identified in Chapter 5. Here, the forward problem is as straightfor
as it was for many of the systems in Chapter 6. Given the setup of the
tem, predict what the particles will do. Details of particle interactions
the nature of the environment and driving force may make this difficult,
the question is posed easily enough and is still relevant. The yield pro
also appears. We could ask, for example, what percentage of the part
initially distributed in the fluid will end up in our ordered chain. We see
Figures 7.2 and 7.3 that the yield is not one hundred percent. Here, it ma
a question of time. How long must we wait to ensure that some suitable
centage of our particles has joined a chain? As usual, the backward pro
is present and is the most difficult to attack. We could ask: How migh
tailor our particle shapes, our choice of fluid, and the geometry of the app
field to form a given dynamic structure? In the remainder of this section
explore various systems that demonstrate the range of possible answers to
question.

7.2.1 Self-Assembling Nanowires

In the system described above the sum of the diameters of all of the parti
used was less than the gap between the electrodes; the particles could not
the gap. This caused the system to enter into a dynamic ordered state wi
the particles oscillated continuously. In the systems we'll consider here, m
more particles are used and linear structures formed can span gaps betw
electrodes. This allows one to self-assemble wires. The wires are still dyna
structures but instead of an oscillating dynamic chain, they form a contin
conducting wire.

In an attempt to create nanoscale wires with novel electrical proper
Bezryadin et al. [13] experimented with graphitized carbon nanoparticle
an electric field. A scanning electron microscope image of their assem
wires is shown in Figure 7.5. To create these wires the group dispersed gra
tized carbon nanoparticles, approximately 30 nanometers in diameter, in
dielectric fluid toulene. The group then used standard lithography techniq
to fabricate a pair of chromium electrodes on the surface of a piece of silic
The electrodes were about 10 nanometers thick and placed about 1 mic
apart. The silicon wafer was then immersed in the toulene solution an
potential difference was applied across the chromium electrodes. The appl

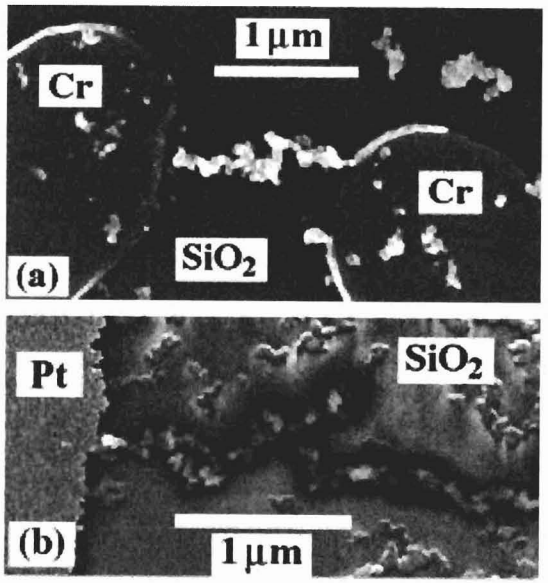

FIGURE 7.5: Scanning electron microscope images of a self-assembled chain of carbon nanoparticles. Reprinted with permission from Bezryadin et al., Applied Physics Letters, v. 74, 1999, pp. 2699. Copyright 1999 by the American Institute of Physics.

potential was 40 volts. In addition, the group placed a large 1 giga-Ohm resistor in series with the voltage source. The presence of the resistor ensured that only one wire formed.

As the system evolved Bezryadin et al. monitored the current. The initially very small current through the system jumped by several orders of magnitude after only a few seconds. In this way, the group knew that a continuous wire had been formed. Since the group could not directly observe their wires during the assembly process they immediately removed their silicon plate from the solution when they observed the current jump. The plate could then be dried and the wire structure preserved. This then allowed them to obtain SEM images of their assembled wires such as the ones shown in Figure 7.5. During their experiments the group managed to grow nanowires as long as 6 microns in length. The bottom half of Figure 7.5 shows a portion of their longest chain. Note that the aspect ratio of their longest wire, the ratio of length to diameter, is approximately 200,000. For comparison, the aspect ratio of a piece of human hair 6 microns long is only about 1/10.

Now, it is important to note that while the basic features of the Bezryadin et al. experiments are the same as those of the large scale system described above, due to scale effects the dominant forces in the assembly process likely differ. Perhaps more important to note is that unlike the toy system above,

the nanowire system of Bezryadin et al. promises to be directly useful i
plications. As mentioned above, one of the primary goals of their work
to fabricate nanowires with novel electrical properties. This possibility a
because the system operates at the nanoscale. At this scale, quantum ef
come into play and the charge transport from particle to particle is affe
In particular, in such systems, the well known Coulomb blockade occur
variety of devices such as the single electron transistor have been designe
the basis of this phenomenon. The reader is referred to [13] for more de
concerning the possible application of nanowires.

In a related set of experiments, Hermanson et al. [61] fabricated micro
wires from suspensions of nanoparticles. However, this assembly process
carried out using AC applied voltages and explicitly relied upon the
nomenon of *dielectrophoresis* (DEP). In DEP particles move because
become polarized by an applied electric field. When a dielectric partic
placed in an electric field there is a nonzero field within the particle. Th
in contrast to a perfectly conducting particle where the internal electric
is identically zero. The presence of an electric field in the dielectric pa
causes charge migration within the particle, resulting in polarization. W
the particle is overall charge neutral, the distribution of charge is such
one end of the particle appears negatively charged and the other positi
charged. Two examples of this appear in Figure 7.6. The dielectric con

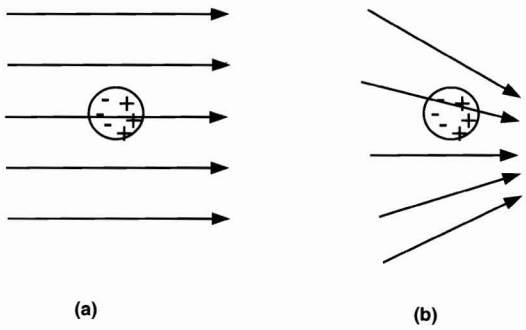

FIGURE 7.6: The behavior of a dielectric particle in a uniform ele
field (a) and a converging electric field (b).

of the material is in fact a measure of the extent to which the material
comes polarized in this situation. If the surrounding field is spatially unif
forces on these charges exactly balance and the particle feels no net force
in the left hand sketch of Figure 7.6. On the other hand, if the surround
field is spatially nonuniform, forces on these charges no longer balance,
the particle feels a net force as in the right hand sketch of Figure 7.6.

simplified situations these forces may be computed exactly. The reader is referred to [101] for further discussion of DEP and a derivation of the exact forces on a dielectric particle with spherical shape.

Here, our main interest is in how Hermanson et al. used DEP in the design of a dynamic self-assembling system. In constructing their system this group used gold nanoparticles between 15 and 30 nanometers in diameter. These particles were suspended in water and the mixture was placed between a pair of planar metal electrodes. The gap between the electrodes could be varied from microns to centimeters in length. The applied alternating potential in these experiments was between 50 and 250 volts, alternating with a frequency of 50 to 200Hz. The results of several of these experiments can be seen in Figure 7.7. In this case, the group could observe the dynamic assembly

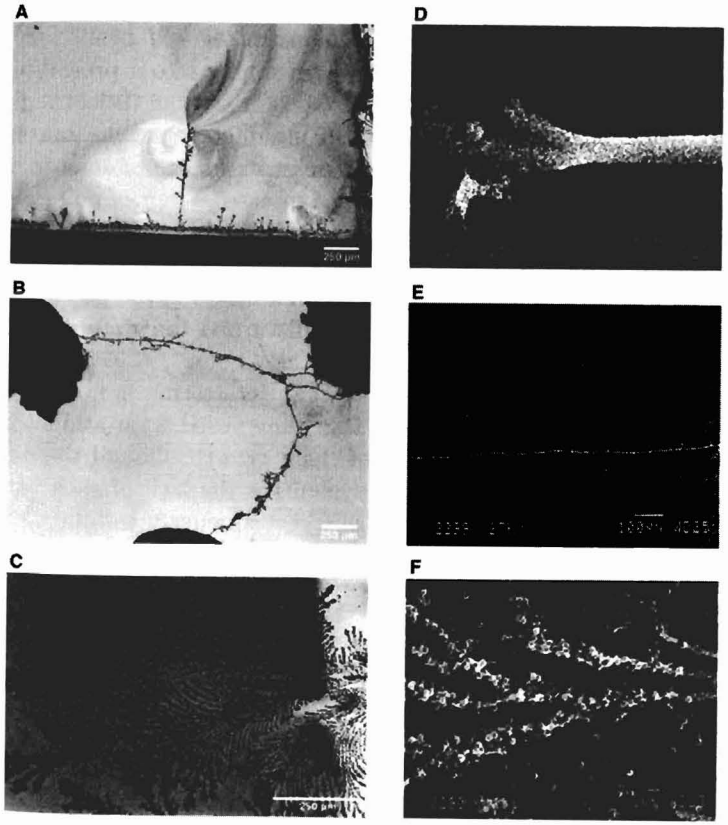

FIGURE 7.7: Images of growing nanoparticle wires from Hermanson et al. From Hermanson, et al., Science, v. 294, pp. 1082-1086, (2001), Reprinted with permission from the AAAS.

process. When the voltage was applied they observed thin fibers growing
the electrode towards the other electrode. The fibers grew at approxim
50 microns per second. The group conjectured that the fiber growth
due to a combination of the DEP effect and complex hydrodynamic e
occurring at the end of the growing wires.

Hermanson et al. were able to achieve a good deal of control over the
ture of their growing fibers by varying several environmental param
They studied the effects of variations in the applied voltage, the AC
quency, particle concentration, particle size, and electrolyte concentrati
their solution. They found that under the right conditions they could a
ble branched wires and systems of interconnects spanning multiple electr
Further, they were able to assemble complicated dendritic structures su
the one shown in Figure 7.7 (c). The group also noted that their struc
were *self-healing*. They demonstrated this by increasing the current thr
an assembled microwire until the wire snapped like a fuse. Quickly, new
ticles moved in to fill the gap and the wire reassembled.

In yet another set of experiments demonstrating self healing of a
Dueweke et al. [35, 127] worked with a system similar to our prototype, b
a different geometry. Their system consisted of a layer of dielectric fluid
petri dish. The diameter of the dish was 140 millimeters and the fluid laye
5 millimeters thick. Metallic spherical particles about 1 millimeter in diam
were deposited in the fluid. The group then inserted a pair of point electr
into the dish and applied a potential difference between the electrodes.
potential used was between 15kV and 25kV. As in the experiments discu
above, the particles moved and formed a chain bridging the gap between
electrodes. Also as above, if the chain was disturbed the system reassemb
and repaired the chain.

What makes the work of Dueweke et al. so interesting is not only the
sults of their experiments but the fact that they posed a variational princ
that appears to govern the dynamics of chain growth. One of the difficul
in modelling dynamic self-assembling systems is the lack of such variatio
principles. In contrast to static systems, where an energy minimization pr
ciple can usually be uncovered, in dynamic system energy is not minimiz
Duewek et al. proposed that their system minimized *resistance*. They defin
the total resistance of their system as the ratio of the applied potential d
ference between their electrodes to the total current flowing between th
electrodes. Then, neglecting inertial forces, they introduced an equation
motion for each particle in the system. In particular,

$$\gamma \dot{\vec{r}}_i = \frac{1}{2\epsilon} \int_S \vec{E}_i^2 da_i \vec{n}_i. \qquad (7.$$

Here, $\vec{r}_i$ is the position vector of the ith sphere, ϵ is the permittivity of t
fluid, γ is a drag coefficient, and $\vec{E}_i$ is the electric field at the surface of the i
particle. The integration is performed over the surface of the sphere. Nex
using the method of images and the principle of superposition, they were ab

to eliminate the field from the right hand side of their equation of motion in favor of a complicated expression only dependent upon the $\vec{r}_i$. In turn, this allowed them to compute the time rate of change of the total resistance in their system. They found that the total resistance was in fact a Lyapunov function for their dynamic equations. That is, the total resistance acted like an energy function for their system and could be shown to decrease with time. At least in the context of this model, their principle of minimum resistance held.

7.2.2 Electrostatically Driven Granular Media

The group led by Igor Aranson has conducted numerous experiments with a system similar to our prototype, but flipped on its side so that particles must also struggle against gravity [6, 7, 116]. Their basic setup is shown in Figure 7.8. Aranson et al. worked with a variety of different experimental

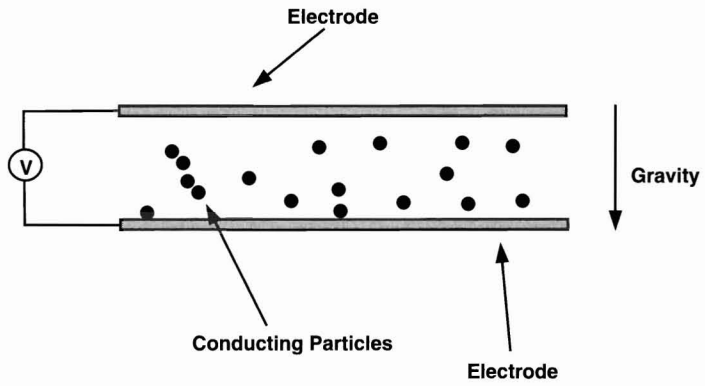

FIGURE 7.8: The basic experimental setup for electrostatic self-assembly when the electric field competes with gravity.

setups, we'll discuss the one described in [6]. In this experiment, 4cm by 6cm plate electrodes were used. The top plate was transparent so that images could be captured from above. The gap between the plates was set at 1.5mm and filled with either air or vacuum. Roughly ten million spherical copper particles 35 microns in diameter were placed in the gap. The team studied both the effects of DC and AC voltage on their system. Voltages of several kilovolts were applied with a frequency ranging from zero to 250Hz.

In this system, when the voltage is first applied all of the particles reside on the lower plate. Since they are in contact with the lower electrode they immediately acquire a charge. The magnitude of this charge depends on the

strength of the applied field. Here, in order to move, the particles must
come the force of gravity, which acts to oppose their initial motion.
does not occur until a critical value of the applied field is reached. Wh
particle does move upward and make contact with the upper plate, it dep
its charge and then falls back towards the lower plate. By applying a
voltage the group found that the height reached by the particles could be
trolled. The switching of the electric field allowed them to push the part
back towards the ground before they made contact with the upper plate

Mapping out the behavior of the system as a function of the applied vol
and frequency the group found three distinct regimes of behavior. In the
regime, no motion occurred. The threshold value of the applied voltage
not yet reached. If the applied voltage was too large the system entered
a phase where the spheres behaved like a granular gas. In this phase,
sphere are dispersed uniformly. The middle or second phase showed the
interesting behavior. The group called this phase the *coarsening* phase. In
state, as particles moved up and down, they also clustered in the horizo
direction. Viewed from above one sees large dots begin to appear. Over
these dots grow and grow together. When examined closely one sees that
particles in these dots are in fact stationary. The particles have formed a t
chain spanning the gap. Remarkably, over time, these dots coalesce and f
one large almost perfectly circular dot. Also within the coarsening regime,
group demonstrated that both the number of clusters and the average clu
radius showed a power law dependence on time. In particular, average clu
radius grew like $\sqrt{t}$ and the number of clusters decreased like $1/t$.

As mentioned above, the Aranson group conducted multiple experim
with the setup described here as well as with variations of this system. U
fluid filled cells the group constructed a system with an even richer ph
diagram. This system formed honeycomb shaped structures, torus sha
vortices and pulsating rings. To truly appreciate these structures the vide
essential. A link may be found in Appendix B.

The dynamic self-assembling system of Aranson et al. nicely illustrates
fact that a range of interesting behaviors can often be observed in a si
system. As is typical, they characterized this range by constructing a ph
diagram for their system. In so doing, they demonstrated how fine con
over the parameters in the system can translate into fine control over
behavior of the system. This represents a partial attack on the backw
problem of self-assembly. Given the characterization of the structures
the system can produce, Aranson et al. showed how to design the system,
tuning of the parameters, to select for a particular structure.

Finally, we note that many other groups have studied systems similar
those described here. The reader is referred to [33, 94] for descriptions of
other particularly interesting studies.

7.2.3 Electrorheological Fluids

If the number of particles in the systems described above is increased by several orders of magnitude, we obtain what is known as an *electrorheological fluid*. As with the ferrofluids described in Chapter 5, the focus of studies with electrorheological (ER) fluids is usually on bulk changes to the rheology of the fluid as opposed to dynamic structures formed by the particles in the fluid. Nonetheless, because of their great potential for applications and their relationship to the systems we've been discussing, we briefly describe ER fluids here.

Electrorheological fluids are easy to make. They typically consist of micron sized particles suspended in a hydrophobic liquid such as mineral or corn oil. A simple suspension of corn starch[5] in corn oil works well. When an electric field is applied to such a mixture the initially randomly distributed particles form chains aligned with the field as in Figure 7.9. That is, the particles behave exactly as the systems we've already encountered in this section. From a

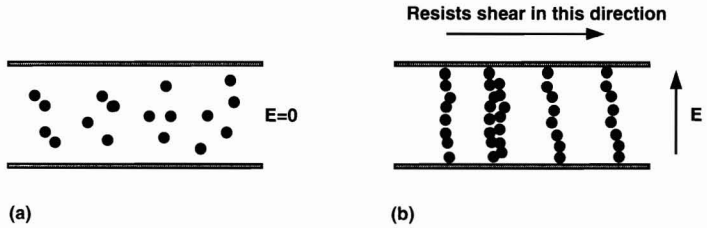

FIGURE 7.9: The behavior of particles in an electrorheological fluid. In (a) there is no applied field. In (b) the applied field causes the system to resist a shear in the direction shown.

technological standpoint, ER fluids are interesting because of the effect chain formation has on the behavior of the system under shear. If the system in Figure 7.9 (a) is sheared, it will behave like an ordinary fluid. If however, we attempt to apply a shear to the system in Figure 7.9 (b), the chains will now play an active role and resist our efforts to slide the top electrode. This type of control over a fluid can be useful in devices such as clutches and active shock absorbers.

From the standpoint of self-assembly there are several features of ER fluids worth noting. First, this is an example of a dynamic self-assembling system. When an electric field is applied, chains form, when the field is switched off, the chains collapse. The system is ordered only when dissipating energy. Next, it is again cooperation and competition between forces that creates order in the system. In ER fluids, electrostatic forces and hydrodynamic forces cooperate

and compete as chains are assembled. Finally, recent studies of ER fluids h
shown that when a field is applied the internal structure of an ER fluid
exhibit more order than simply the formation of chains. In [137, 138]
and Lu demonstrated that net-like structures, reminiscent of a cross-lin
polymers, could be formed. They further showed that by varying the surf
properties of the particles suspended in the fluid, the patterns formed co
be controlled. The reader is referred to [137, 138] for further details.

7.3 Magnetically Driven Dynamic Systems

In the systems of the previous section, electrostatic forces, in competitio
cooperation with gravitational and hydrodynamic forces, led to dynamic
self-assembled structures. In this section, we focus on systems where *magn*
and hydrodynamic forces cooperate and compete in the formation of dyna
self-assembled structures.

Here, we will describe aspects of the sequence of studies carried out
George M. Whitesides, Bartosz A. Grzybowski, and various collaborators
reported on in [55, 56, 57, 58]. The basic experimental setup used in [55, 56,
is shown in Figure 7.10. In these studies millimeter-sized magnetic di

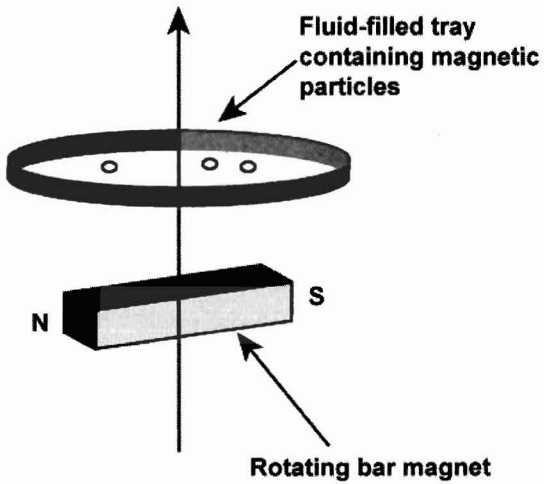

FIGURE 7.10: The experimental setup for the magnetically driven d
namic self-assembling system.

were fabricated and placed in a circular fluid filled tray. The fluid was non-magnetic; a typical choice of fluid was a water and glycerine mixture. A permanent bar magnet was placed below the disk and aligned so that a line drawn through its center would pass through the center of the dish. The magnet was then rotated about this axis.

When the magnet was not moving, the particles in the fluid did feel a magnetic force. In this case, they would be attracted towards the poles of the magnet and would cluster in the fluid at a point above these poles. There they would remain forming largely disordered aggregates. Once the magnetic bar was set in motion the system came alive. Instead of being attracted to the poles as with the stationary magnet, the rotating magnetic field attracted the particles towards the axis of rotation. In addition, the magnetic particles became entrained to the rotation of the bar and began spinning about their centers. The rotation of the particles set the surrounding fluid in motion and created a repulsive hydrodynamic force between the particles.

The rotation of the magnet and its subsequent effects on the particles and the fluid in the tray endowed this system with the properties needed to dynamically assemble interesting structures. The magnetic forces were cooperative, drawing all of the particles towards the center of the tray. The hydrodynamic forces were competitive, pushing nearby particles apart. By changing the numbers of particles in the system the group was able to create a variety of dynamic structures. Sketches of these structures are shown in Figure

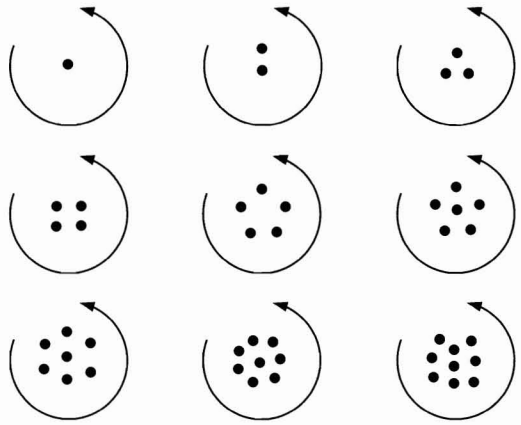

FIGURE 7.11: Dynamic patterns formed in the rotating magnetic disk system.

7.11. Note that when a single particle was used, it migrated to the center and rotated. When more than one particle was used, mutual repulsion between

the particles balanced with the magnetic attraction towards the center. T
forced the particles into a variety of geometric patterns. These patterns
tated as a whole about the center of the tray. The group also found tha
certain values of the number of particles more than one dynamic struc
was possible. When ten, twelve, or nineteen particles were used two diffe
dynamic states were observed. For the cases of ten or twelve particles the
tem spontaneously switched between these states. When nineteen part
were used, the states were segregated by a threshold value of the rotati
speed of the bar magnet. Finally, the group also showed that the spa
between the disks was only a function of the angular speed of the bar mag
This indicates that the magnetic force on a particle was independent of
number of particles but that the hydrodynamic repulsive force increased
the particle's increasing angular speed.

In [58] the group extended the basic experimental setup of Figure
and showed that a modified version could be used to produce self-assemb
micro-fluidic machines. This time, in addition to a rotating permanent m
net, the group embedded an array of electromagnets beneath the fluid l
in the tray. These electromagnets could be controlled by the user. They
modified the disk shaped particles of their previous experiments, this
creating small rotors. As before, when the permanent magnet was set
motion, the rotors were attracted towards the center of the tray, individu
rotated, and repulsed one another via hydrodynamic forces. However, h
once a dynamic structure had formed it could be further manipulated u
the embedded electromagnets. The group fabricated three different fu
tioning machines using this approach. In one of their machines seven ro
and nineteen electromagnets were used. By activating the electromagnets
group could freeze the rotors into the structure shown in Figure 7.12 (c). N
that each rotor continues to spin even when the overall structure is locke
place. This means that a flow is created in the fluid. It was this flow that
group sought to manipulate and use to build a working device. The act
of their rotary "carousel" system is shown in Figure 7.12. Note the prese
of a small circular container in these figures. When the carousel was loc
in place with all of the rotors spinning, the container remained outside of
carousel. By selectively activating the embedded electromagnets, the gr
could break the array and cause the container to move to the interior of
carousel. This is shown in Figure 7.12 (b) and (c). The carousel then mo
the container around the central axis till it reached the point shown in Fig
7.12 (e). Here, a small syringe filled the container with a dyed fluid. T
carousel then moved the container up to the point shown in Figure 7.12
finally ejecting it back into the bulk fluid. The carousel array was then b
in its original configuration and ready to process additional containers.

The systems described in this section serve as another nice example
an engineered dynamic self-assembling system. Here, the role of both t
attractive magnetic forces and the repulsive hydrodynamic forces is clear.
particular, these systems illustrate how system variables can be manipula

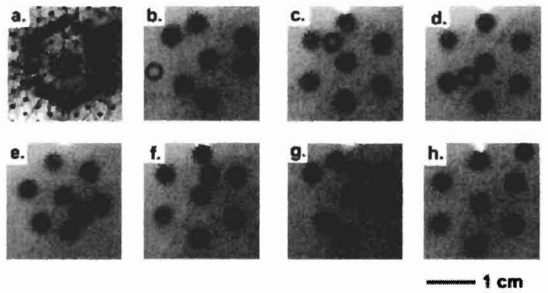

FIGURE 7.12: A self-assembling micro-fluidic machine. (a) shows the array of 19 electromagnets used in the system. Parts (b) through (h) show the system acting as a pump. The empty container is drawn into the array in (b), it is filled by (e) and ejected in (h). Reprinted with permission from Grzybowski et al., Applied Physics Letters, v. 84, 2004, pp. 1800. Copyright 2004 by the American Institute of Physics.

to create different dynamic patterns. It is interesting to compare the system described here with the system of Stambaugh et al. described in Chapter 5. According to our definition, the Stambaugh system, although static in its assembled state, is an example of dynamic self-assembly. Recall that the Stambaugh system used an externally applied magnetic field to confine a set of magnetic particles. When the magnetic field was switched off, the system collapsed from an ordered dynamic state to an ordered static state. This is similar to what we've seen above. Here, when the permanent magnet is not rotating, the system migrates towards a somewhat ordered static state. When the magnet is set in motion, the system switches to a dynamic state. The key difference between the system of Stambaugh et al. and the systems of this section is the addition of a second significant force to the system. In particular, the systems of this section made use of repulsive hydrodynamic forces. This added a layer of structure not present in the system of Stambaugh et al.

7.4 Mechanically Driven Dynamic Systems

Systems of particles suspended in a fluid can be vibrated electrostatically and magnetically. They can also simply be shaken. This mechanical driving of granular fluids brings us into contact with the vast area of research into the nature of granular media. Here, we briefly describe two simple studies closely related to the other systems considered in this chapter. The reader is directed to the Related Reading section at the end of this chapter for an introduction

to the field of granular media and pointers to the enormous body of litera
on this subject.

The first system we'll consider is due to Voth et al. [135]. The setup of
experimental apparatus is very similar to the apparatus used by the Ara
group pictured in Figure 7.8. The Voth et al. setup for mechanical shakin
shown in Figure 7.13. This group suspended tiny stainless steel spheres

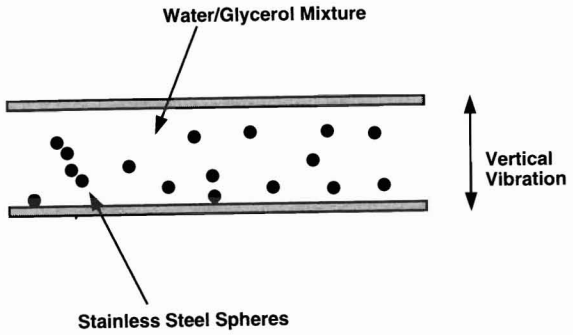

FIGURE 7.13: The experimental apparatus for the vibrated granular
tem.

mixture of water and glycerol. The radius of the spheres was approxima
0.4mm. The mixture filled a short, fat, cylindrical aluminum tank. The t
was about 6cm in diameter and about 1.5cm in height. The top of the t
was sealed with a glass window so that high speed video could be captu
from above. The entire apparatus was placed on an electromagnetic vibra
Both the frequency and amplitude of the vibrations could be controlled.

As with previous systems, when there was no applied force, the partic
simply distributed themselves randomly on the bottom plate. When the
brator was turned on the particles hopped up and down, typically strik
the bottom cell once each cycle. When a large number of particles was us
the group observed coarsening behavior like that in the electrostatic syst
examined earlier in this chapter. The initially randomly distributed partic
clustered together and the clusters slowly coalesced into a large superstr
ture. To explain this behavior the group identified a hydrodynamic attract
force operating between the particles. Modelling the flow around a sin
particle, they showed that there was a steady inflow of fluid towards
equator of each particle. This inflow provided an attractive hydrodynam
force. The group also identified the presence of a hydrodynamic repulsi
force in the system that acted only when large accelerations were applied
the electromagnetic vibrator. Using flow visualization techniques, they we
able to observe recirculation zones near the particles. They speculated th

the observed repulsive force was due to these recirculation zones, but could not demonstrate this conclusively.

The observation that the system could produce both attractive and repulsive forces led the group to study the behavior of systems consisting of only a handful of particles. When three particles were used, they anticipated that the particles would form a stable triangular structure in much the same way as the magnetic system of Section 7.3. However, the particles did not quite behave. When accelerations were low, a nearly triangular shape formed. But, when accelerations were increased, the system transitioned to a state with two particles clustered and the third particle dancing about in the distance. On occasion the third particle would wander back to the pair, ask for a turn to dance and form a new cluster while one of the previously paired particles was ejected into the distance. When seven particles were used the system again exhibited an acceleration dependent transitional behavior. For low accelerations, the group observed stable hexagonal structures. When accelerations increased, the structure again became time dependent with two central particles dancing inside a ring comprised of the five others. As with other systems described in this chapter, video is essential to fully appreciate the system's behavior. A link may be found in Appendix B.

The second mechanically driven dynamically self-assembling system we'll discuss is due to the group led by Harry L. Swinney. Details of this system may be found in [92]. In some sense, this group simply took a typical electrorheological fluid and shook it vertically. Remarkably, this led to fascinating behavior. The team worked with two different fluid mixtures. The first was a simple suspension of cornstarch in water. The second was a suspension of glass microspheres, of diameter between one and twenty microns, dispersed in water. In either case, the fluid was placed in a circular dish about 9.4cm in diameter. The cornstarch was poured to a depth of 0.5cm, the glass spheres were poured to a depth of 0.2cm. The top of the container was sealed with a clear glass plate and images were taken from the top. As above, the entire apparatus was placed on a mechanical shaker. The frequency and amplitude of the vibrations could be adjusted.

When the shaker was turned on the group observed a striking range of patterns on the surface. Most notable was the presence of persistent holes in the fluid. These holes, or cylindrical vacancies, penetrated entirely through the depth of the fluid and could last for the lifetime of the experiment. To better understand this phenomenon, the group mapped out a phase diagram for the system. Here, the different behaviors are a function of the forcing frequency and acceleration. When the acceleration was low, holes were unstable. They found that they could initiate hole growth by shooting a puff of air towards the surface of the fluid but that these holes would rapidly close. For larger accelerations, and the right choice of frequency, the group identified regions of the phase diagram where holes would form, adjust to a well-defined size, and persist. In still other regions of the phase diagram, the group observed what they called "delocalized" behavior. In this region, holes would form a

hump on their upper rim. This hump would grow out of the fluid like a fi eventually reach a maximum height, and then topple back into the fluid. toppling excited other regions of the fluid and eventually the entire su was filled with evolving voids and vertical structures. Again, video is e tial to truly appreciate this genuinely weird behavior. A link may be f in Appendix B.

7.5 Self-Propelled Systems

In the systems we've considered thus far, the driving force has come an *externally* applied field. In the system described in this section, the interaction of structured particles with the environment that provide driving force. This system is yet another creation of the Whitesides group and was inspired by complex biological systems such as swarming bacteria schooling fish. Their intent was to capture the complex behavior exhi by large collections of independent agents in an engineered self-assem system.

The group began by fabricating PDMS tiles as in their previous stu Once again, the hydrophobic and hydrophilic properties of the tiles cou tailored. This time, an additional modification was made to the tiles. Eac was outfitted with a small platinum coated glass "fin." This fin was ori perpendicularly to the face of the tile and attached to the tile by a steel pi sketch of the tiles appears in Figure 7.14. The tiles were placed on the su of a liquid. Here, the liquid was a mixture of water and hydrogen pero The platinum fin was immersed in the liquid while the upper face of th remained in the air. When the fin made contact with the hydrogen per solution, the platinum coating catalyzed the decomposition of the hydr peroxide into water and oxygen. This caused small gas bubbles to form a fin surface. The ejection of these bubbles from the fin provided a locom force for the particle. The group found that their fin equipped particles c continue to move with almost constant velocity for several hours.

Note that the shape of the particles in Figure 7.14 lacks symmetry. implies that when propelled through the hydrogen peroxide solution the ticles will rotate. In their experiments, the Whitesides group used part shaped like those in Figure 7.14 and particles with the same shape, but fli upside down. This meant that their system contained particles that s both clockwise and counterclockwise. The wetting pattern around the e of the particles was designed so that particles could bind pairwise. Wo with a single pair of particles, chosen to swim in opposite directions, found that stable binding did occur. The pair formed a two particle com that remained connected and rotated. When a collection of ten particles

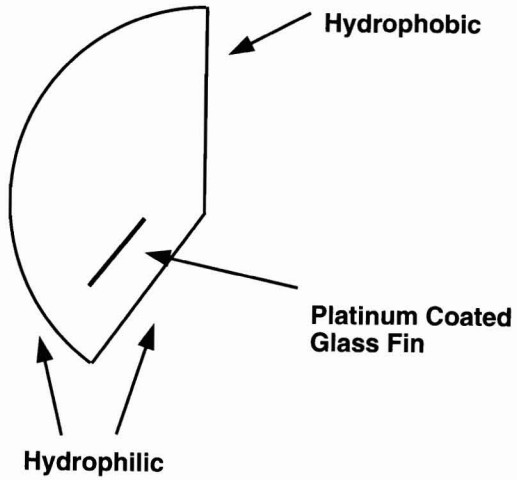

FIGURE 7.14: Design of self-propelled particles. This is a view from the bottom. The platinum coated fin is immersed in the liquid layer.

used, the particles still formed stable particle pairs, but not with one hundred percent yield.

The system described here constitutes a proof of concept. The Whitesides group was able to demonstrate that it was possible to design a dynamic self-assembling system without using an externally applied field. Unfortunately, they have not yet been able to carry out experiments using large numbers of their self-propelling particles. They speculate that such experiments will lead to more complex emergent behavior. Simulations of such systems support this speculation. For one such study the reader is directed to [29].

7.6 Smart Particles

The systems of this chapter as well as those of Chapters 5 and 6 are quite impressive. But, we must face one fact. All of the particles used in all of our clever engineered self-assembling systems are *dumb*. We may give them fancy names like "structured particles," we may paint them with hydrophobic and hydrophilic stripes, we may give them pretty shapes and decorate them with magnets. But, they're still dumb.

In sharp contrast, nature's particles are *smart*. When we discussed proteins in Chapter 3, we described how a protein folds and adopts a particular conformation. Proteins are also able to change shape, that is, change this con-

formation, in response to interactions with other proteins or the environm
We saw this behavior in the tobacco mosaic virus when self-assembled pr
washers switched to a lock-washer geometry in response to interaction
RNA. We call this behavior *conformational switching*. This change in s
allows nature's particles to change how they bind and how they interact
the environment. Nature's particles are smart.

Now, to be fair, we have seen some particles that can undergo confo
tional changes. For example, in the electrostatic systems of this cha
particles were able to change their state by changing their charge. But,
don't do so intelligently. Yes, they do change in response to other part
and they do change in response to the environment, but they are mere pa
participants in this process. In contrast to particles like the TMV disk
teins, that only change conformation when the right strand of RNA app
these particles still appear dumb.

So, how do we move towards engineered systems that use smart parti
One approach to this has been pioneered by Eric Klavins [14, 73] and wi
discussed in this section. However, before we examine the Klavins sys
let's revisit some of our earlier self-assembling systems and see what feat
smart particles might have and how they might help us design better syst

First, let's consider how smart particles might help us build better syst
Imagine we returned to one of the tile based systems of Chapter 6 and
structed a set of triangular tiles like those shown in Figure 7.15. We'll ass

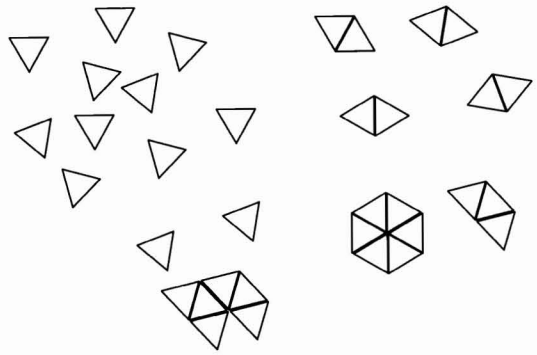

FIGURE 7.15: A collection of self-assembling triangles forming differ
shapes.

that all of the edges are capable of binding. We might accomplish this magi
ically or by using the wetting properties of our tiles. If we placed our trian
in the proper environment, we'd see them start to form triangle comple
like those shown in the figure. We'd see triangle doublets appear, triple

chains, and perhaps even hexagonal structures. But, suppose our goal was to form only hexagons? Well, in this system, we'd be faced with a serious yield problem. We might obtain a few hexagons, but our experience with similar systems in Chapter 6 leads us to believe that our yield would be low indeed. Now, we have developed some tools to help us attack this problem. We could turn to the use of templates, we could change the patterns of binding forces on the particle edges, or we could tinker with our particle shapes. Each of these approaches would yield some success. But, now suppose our goal was more ambitious. Suppose we wanted to force all of the triangles to form hexagons, remain in this state for some period of time, and then return to a state of unbound triangles. The techniques we've see thus far are no longer of much help. We could attempt to use some of the ideas outlined in this chapter to build such a system, but wouldn't it be much simpler if somehow our particles could decide what state they were in and make the switch from hexagons to triangles on their own? Wouldn't it be nice if our particles were *smart*? If the triangular particles of Figure 7.15 were smart, they could perhaps sense what sort of structure they were bound to and decide on their own to remain bound or not. Endowing our particles with such an ability would clearly make the design of dynamic self-assembling systems much easier.

Let's consider this concept of smart particles in yet another context. Recall that in Chapter 2 we discussed the process of polymerization. Let's imagine a highly simplified polymerization process that consists of polymers of only three lengths. We can imagine polymer chains consisting of one, two, or precisely three monomers as being the elements of our system. We'll pretend that no catalyst is needed for our system and simply assume that two simple reactions govern our polymerization process. Namely,

$$\begin{aligned} P_1 + P_1 &\longrightarrow P_2 \\ P_1 + P_2 &\longrightarrow P_3. \end{aligned} \tag{7.2}$$

Using the Law of Mass Action we can write down equations governing the concentrations of our reactants. Assuming a reaction rate of k for all reaction we find that the concentrations, denoted by $p_i(t)$, satisfy

$$\begin{aligned} \frac{dp_1}{dt} &= -kp_1^2 - kp_1p_2 \\ \frac{dp_2}{dt} &= kp_1^2 - kp_1p_2 \\ \frac{dp_3}{dt} &= kp_1p_2. \end{aligned} \tag{7.3}$$

Even though this system is nonlinear, it is not hard to see how the p_i evolve. Clearly, p_1 only decreases and p_3 only increases. The behavior of p_2 depends on initial conditions, but, even if p_2 increases initially it will eventually tend toward zero. This is not surprising. Our reactions say that the p_1's combine to form p_2's, the p_2's combine with p_1's to form p_3's, and nothing else can happen.

Profile - Eric Klavins

Some people use air hockey tables to play air hockey, Eric Klavins u
as a platform for his army of programmable self-assembling robots. K
an electrical engineer at the University of Washington, is a member of t
generation of self-assembly pioneers, taking a classical education in co
science and engineering and applying it to the difficult and challengi
of designing and building nontrivial self-assembling systems. In 200
received a prestigious National Science Foundation Career Award base
work in programmed robotic self-assembly. Since then, Eric and his gr
student, Nils Napp, have built triangular, programmable robotic "part
live on an air hockey table, randomly mixing, and self-assemble into
structures. The parts bind magnetically and are endowed with the ab
communicate with one another and make decisions concerning bindin
on a locally stored graph grammar. Eric has been a leader in using
grammars as a tool to model and control self-assembly. Photos of the K
robots are shown below while fascinating videos of the assembly proc
available on his web page. The link may be found in Appendix B.

In a recent conversation, Eric commented on the blind-spots holdin
development in the field of self-assembly. He writes:

> *I think we keep confronting massive combinatorial state spaces tha
> lack convenient models. Low level models are too complex, whil
> continuum models miss the details. People avoid systems that gen
> erate such state spaces and focus too much on simple self-assembly
> essentially crystallization. We need to focus on the fundamentall
> new algorithmic possibilities of self-assembly.*

Currently, Eric and his group are extending their approach to MEM
DNA self-assembly. They are working to apply their ideas about
programmable assembly, developed on their air hockey table, to micr
nanoscale systems.

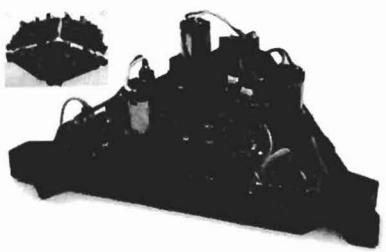

FIGURE 7.16: Eric Klavins' self-assembling robotic parts. The
shows a self-assembled structure. Credit: Eric Klavins and Nils Napp.

Eventually, most of what we form must be polymers of length three. But suppose that what we really wanted was to form polymers of length two. Then, we'd again be faced with a yield problem. We saw in Chapter 2, that the distribution of polymer lengths evolved with time. The same is true here. We could analyze our system in more detail and then stop the polymerization process at the instant when the yield of the p_2's was maximized. But, if our particles were smart, we could increase our yield of p_2's and avoid worrying about precisely when to stop the process.

To see how this might work, imagine that each of our monomers was able to sense its state. That is, suppose periodically, each monomer checked whether it was still a monomer, a dimer, or a trimer. Further, assume that each particle could make a decision about its binding based on the state identified. If a particle found it was a monomer or a dimer, we'd want it to do nothing. If however, it found it was part of a trimer, we'd like it to unbind and destroy the trimer. However, there is a complication. If all of the subunits simultaneously decide to unbind, we'd produce monomers when we could be producing the desired dimers. So, in addition to being able to identify their state, we want our particles to communicate and somehow mutually decide what to do. For the polymerization system we wish to add a new reaction pathway that Klavins calls a *programmed reaction pathway*. For our system this is

$$P_3 \longrightarrow P_1 + P_2. \tag{7.4}$$

If we included this reaction and assumed it occurred at some programmed rate, k_p, our system of differential equations would become

$$\begin{aligned} \frac{dp_1}{dt} &= -kp_1^2 - kp_1p_2 + k_pp_3 \\ \frac{dp_2}{dt} &= kp_1^2 - kp_1p_2 + k_pp_3 \\ \frac{dp_3}{dt} &= kp_1p_2 - k_pp_3. \end{aligned} \tag{7.5}$$

Now the behavior of our system is closer to what we desired. The concentrations of p_1 and p_3 no longer evolve monotonically. Rather, the breakup of the p_3's ensures that new p_1's are produced eventually leading to the desired p_2's. Note that this system can be optimized by choosing k_p. We invite the reader to investigate this further in the exercises for this section.

The protocol outlined above, that is, the use of particles that can both sense their state and collectively make decisions about binding, was implemented by Eric Klavins et al. in [14, 73]. Klavins et al. designed triangular programmable particles and allowed them to mix and interact on an air-hockey table. A photograph of one of the team's particles appears in Color Plate 11.11. Each triangular particle contained three controllable magnetic latches, three infrared transceivers, and a logic circuit. The latches and transceivers were arranged symmetrically so that the triangular parts could bind as in our thought experiment of Figure 7.15. Binding was accomplished via the use of permanent

magnets. Each magnetic latch on the particle actually consisted of three manent magnets. One of these, the central magnet, was fixed in place its north face protruding outwards from the particle. Surrounding this two movable magnets whose position could be adjusted by a motor. In default state, the two movable magnets point with their south faces f outwards. When two particles come sufficiently close, they bind. The magnet of one particle will attach itself to one of the movable magnets o other particle. However, particles could unbind. If a pair of particles de to unbind, they would each use an onboard motor to rotate their mo magnets by 180 degrees. This would force the particles apart. The mov magnets would then return to the default state, allowing each particle to bind freely.

In addition to the mechanical ability to bind and unbind, the particles needed to be able to sense their state, communicate with their neighbors, collectively make decisions about binding. To implement this aspect of smart particle design, each particle was equipped with a logic circuit an infrared transceiver. The transceiver allowed particles to communicate. logic circuit allowed the particles to decide whether or not to remain bo The circuit made decisions based on a *graph grammar*. Graph grammars re sent a powerful approach towards understanding and modelling self-assem We'll revisit graph grammars in Chapter 9. Here, we simply note that particle defined its state in terms of the position of its three latches. state and the states of nearby neighbors were then examined by the circuit. The logic circuit essentially translated these states into the langu of a predefined graph grammar, examined the graph grammar to deter how to act, and communicated this information back to the latches. No that the particles were programmable. The graph grammar by which the l circuits made decisions was stored in each particle's internal memory. this graph grammar could be changed and hence this system really achie *programmable* self-assembly. In [73], Klavins et al. showed how to specify ferent graph grammars to achieve different assembly goals. In fact, they showed how to specify a graph grammar so that their robotic triangles wo self-assemble into the hexagonal structures we originally considered at start of this section.

7.7 Chapter Highlights

- Dynamic self-assembling systems are those that produce ordered str tures that remain ordered only so long as the system is dissipating ergy.

- For dynamic self-assembly to occur their often must be a competition between particle interaction forces. In our prototype system, particles are electrically charged and can hence attract or repel. Charged particles can change their charge and hence change how they interact with other particles.
- The competitive and cooperative efforts of electrostatic, hydrodynamic, and gravitational forces in a particle-fluid system can lead to the formation of one, two, and three dimensional spatial and temporal structures.
- Magnetic forces in competition with hydrodynamic forces may also be used to create dynamic self-assembling systems. This competition can be used to create structures consisting of only a handful of particles, or massive structures capable of changing the bulk behavior of a fluid.
- Dynamic self-assembling systems may also be formed using purely mechanical driving. Here, it is a complex interaction of attractive and repulsive hydrodynamic forces that gives rise to structure.
- The use of an externally applied driving force may be avoided by creating particles that are *self-propelling*. These particles interact with their environment to produce a motive force. Experiments with self-propelling particles may yield insight into collective biological behavior such as swarming and schooling.
- To truly approach the abilities of nature we must turn to *smart particles*. Smart particles mimic proteins and are able to undergo *conformational changes* in response to other particles or the state of the environment.

7.8 Exercises

Section 7.2

1. Consider a single conducting particle in a dielectric fluid placed between two electrodes. Assume the electrodes are parallel infinite plates. Assume the effect of the particle on the field is negligible and compute the electric field in the gap. Now, use this to write down an equation of motion for the particle. Include drag forces on the particle in your model. You may assume the particle is spherical so that Stokes' Law applies. Under what conditions will the inertial terms be negligible?
2. Repeat the problem above but this time include the effect of gravity. Assume that the gravitational force points in a direction perpendicular to the electrodes. How much charge must a particle acquire if it is to be able to move upwards against the force of gravity?