

PATTERN FORMATION IN DIBLOCK COPOLYMERS

DMITRIY L. KOGAN

INTRODUCTION

Polymers are long molecules composed of many smaller units called monomers. Generally, polymers are flexible and can bend at the monomer junctions. Diblock copolymers are a type of polymer that is composed of a long chain of one monomer, followed by a long chain of another monomer. So if a diblock copolymer is composed of monomers A and B , its chain would look like $A-A-\dots-A-B-\dots-B-B$. The chemical process that is the basis for this research is the deposition of a Polystyrene-Polyethyleneoxide (referred to as PS-PEO from this point on) diblock copolymer solution (dissolved in chloroform) onto a water surface. The self-organized patterns that form at the air-water interface as a result are the subject of the modeling.

The PEO part of the polymer is hydrophilic so contact with the water surface decreases the free energy of the PEO. Thus the PEO part of the polymer organizes as a flat pancake at the interface. On the other side of the polymer, the PS is hydrophobic so water contact is not preferable for it. Thus the PS sticks out of the PEO pancake like a tail. So when the polymer solution is deposited onto the water surface, the molecules move around on the surface because of diffusion and surface tension effects. The PS tails get entangled during this movement and as the solvent evaporates, the whole system slows down. Soon, the patterns are fixed. When this happens, the whole system is compressed to a particular surface pressure in the Langmuir-Blodgett trough where the whole process takes place. Here, we never compress the system enough for the PEO pancakes to interact with each other. So brushes (3D structures caused by the subduction of the PEO) are never observed. This is thus a 2D problem. After the compression, the patterns are deposited on a substrate and imaged.

Depending on the parameters, we can get dots, spaghetti or continents. Some example experimental images are in Figure 1 (from [3]).

MODEL

We have 4 main effects that we need to include in the model. These are

- (1) Diffusion
- (2) Surface tension
- (3) Solvent evaporation
- (4) Entanglement

Let's model these one at a time.

Diffusion. When the solution is deposited onto the water, the polymers experience diffusion forces which move them from regions of high concentration to low concentration. This happens due purely to random motion of the molecules, thus it can be modeled by the standard diffusion equation:

$$\frac{\partial c}{\partial t} = D\nabla^2 c$$

where c is the concentration of the solution, t is the time, and D is the diffusion constant. This is a stabilizing effect so $D > 0$.

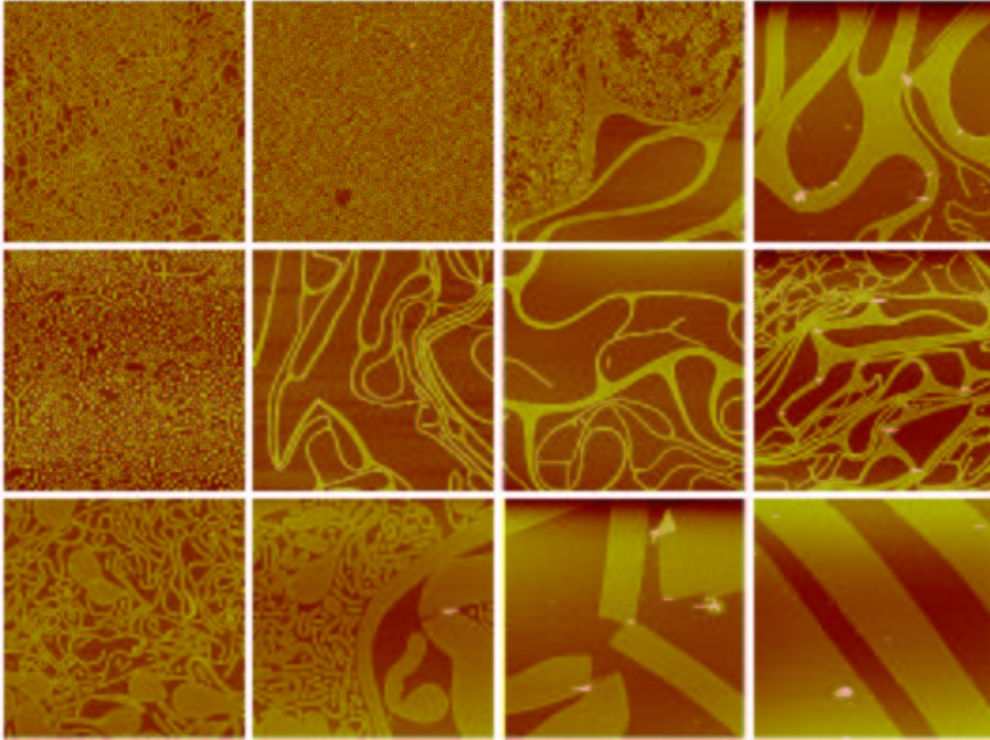


FIGURE 1. These are sample microscope photographs illustrating experimental results. Here we see dots, spaghetti and continents.

Surface Tension. The polymers act as surfactants which means that they lower the surface tension around them. Surface tension forces tend to move particles from areas of low surface tension (high concentration, in this case) to areas of high surface tension (low concentration, in this case). So we can say that $\mathbf{v} = -k_{\text{surface tension}} \nabla c$ because not only would the polymers move in the direction of dropping concentration, but also move there faster for larger concentration gradients.

Solvent Evaporation. The solvent is what gives the system its mobility. As the solvent evaporates, the movement becomes more and more stiff. Thus the evaporation can be modeled by multiplying the velocity vector \mathbf{v} of the system by a mobility envelope. An exponential envelope of $e^{-\beta t}$ was used where β is a positive constant that models the evaporation rate.

Entanglement. This is the most complicated effect and also one that defines the system. There are many ways of looking at this. One can use a potential function of binary interactions to complete the model, one can use statistical thermodynamics and treat the whole system as an entangled block of polymers, or one can model entanglement using a mean field theory like SCMF (single chain mean field). The current model uses a potential function.

Let's say that two polymers are separated by a distance x . The PS tails of each polymer randomly coil up above the water. The lowest free energy is achieved in the state of highest entropy so there's a preferred length of the tail from start to end. Let $f(x)$ be a function that describes the force that one polymer feels due to another polymer a distance x away. Logically, f would look something like Figure 2. The force goes to 0 as x gets large because the tails have a limit to how far they can stretch. There's a stable distance where there's no force that corresponds to maximum entropy. Overall, this is a restoring force that prefers maximum entropy so we can think of the PS polymer tails as non-hookean springs.

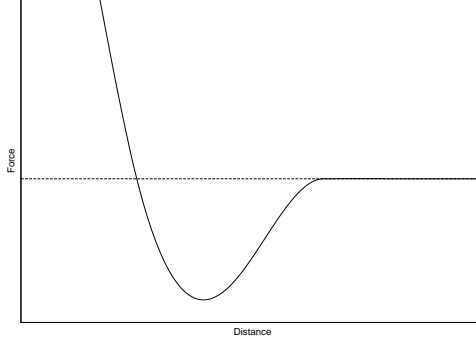


FIGURE 2. This is a sketch of a binary force function. The PEO pancakes would push apart for very small separations; there's a stable distance that corresponds to maximum entropy, and force goes to 0 for large separations.

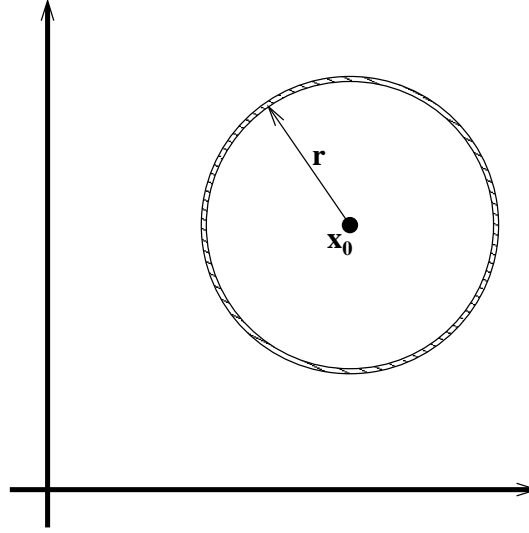


FIGURE 3. This is a diagram illustrating how the model PDE is derived.

Let's find the total force that a polymer at \mathbf{x}_0 feels due to a ring of polymers around it at a distance $|\mathbf{r}|$ away, as shown in Figure 3.

$$\mathbf{F}_{\text{ring}}(\mathbf{x}_0, |\mathbf{r}|) = \int_{\text{ring}} f(|\mathbf{r}|) c \left(\mathbf{x}_0 + |\mathbf{r}| \begin{bmatrix} \cos \theta \\ \sin \theta \end{bmatrix} \right) \frac{\mathbf{r}}{|\mathbf{r}|} d\theta$$

We scale the force with concentration because areas of higher concentration would contain more polymers and would thus exert a greater force. We can break up this force expression using Taylor's theorem to get

$$\begin{aligned} \mathbf{F}_{\text{ring}}(\mathbf{x}_0, |\mathbf{r}|) = & \frac{f(|\mathbf{r}|)}{|\mathbf{r}|} \int_0^{2\pi} \mathbf{r} [c(\mathbf{x}_0) + \\ & |\mathbf{r}| \cos \theta \frac{\partial c}{\partial x}(\mathbf{x}_0) + |\mathbf{r}| \sin \theta \frac{\partial c}{\partial y}(\mathbf{x}_0) + \\ & \frac{1}{2} |\mathbf{r}|^2 \cos^2 \theta \frac{\partial^2 c}{\partial x^2}(\mathbf{x}_0) + |\mathbf{r}|^2 \sin \theta \cos \theta \frac{\partial^2 c}{\partial x \partial y}(\mathbf{x}_0) + \frac{1}{2} |\mathbf{r}|^2 \sin^2 \theta \frac{\partial^2 c}{\partial y^2}(\mathbf{x}_0) + \\ & \frac{1}{6} |\mathbf{r}|^3 \cos^3 \theta \frac{\partial^3 c}{\partial x^3}(\mathbf{x}_0) + \frac{1}{2} |\mathbf{r}|^3 \cos^2 \theta \sin \theta \frac{\partial^3 c}{\partial x^2 \partial y}(\mathbf{x}_0) + \frac{1}{2} |\mathbf{r}|^3 \cos \theta \sin^2 \theta \frac{\partial^3 c}{\partial x \partial y^2}(\mathbf{x}_0) + \frac{1}{6} |\mathbf{r}|^3 \sin^3 \theta \frac{\partial^3 c}{\partial y^3}(\mathbf{x}_0) + \dots] \end{aligned}$$

We know that $\mathbf{r} = |\mathbf{r}| \begin{bmatrix} \cos \theta \\ \sin \theta \end{bmatrix}$ so the terms with even derivatives cancel and we get

$$\mathbf{F}_{\text{ring}}(\mathbf{x}_0, |\mathbf{r}|) = \pi |\mathbf{r}| f(|\mathbf{r}|) \begin{bmatrix} \frac{\partial c}{\partial x}(\mathbf{x}_0) + \frac{1}{8} |\mathbf{r}|^2 \left(\frac{\partial^3 c}{\partial x^3}(\mathbf{x}_0) + \frac{\partial^3 c}{\partial x \partial y^2}(\mathbf{x}_0) \right) \\ \frac{\partial c}{\partial y}(\mathbf{x}_0) + \frac{1}{8} |\mathbf{r}|^2 \left(\frac{\partial^3 c}{\partial y^3}(\mathbf{x}_0) + \frac{\partial^3 c}{\partial x^2 \partial y}(\mathbf{x}_0) \right) \end{bmatrix}$$

Now we can obtain an expression for the total force experienced by a polymer at \mathbf{x}_0 :

$$\mathbf{F}(\mathbf{x}_0) = \int_0^\infty \mathbf{F}_{\text{ring}}(\mathbf{x}_0, |\mathbf{r}|) d|\mathbf{r}|$$

Using the first few terms of Taylor's theorem, we assumed a small $|\mathbf{r}|$, but here we're integrating to $|\mathbf{r}| \rightarrow \infty$. The reason we can do this is because as $|\mathbf{r}| \rightarrow \infty$, $f(|\mathbf{r}|) \rightarrow 0$. So the contribution to the integral for large $|\mathbf{r}|$ will be negligible.

Let's define parameters

$$\begin{aligned} \phi_1 &\equiv \pi \int_0^\infty |\mathbf{r}| f(|\mathbf{r}|) d|\mathbf{r}| \\ \phi_3 &\equiv \frac{\pi}{8} \int_0^\infty |\mathbf{r}|^3 f(|\mathbf{r}|) d|\mathbf{r}| \end{aligned}$$

So

$$\mathbf{F}(\mathbf{x}) = \begin{bmatrix} \phi_1 \frac{\partial c}{\partial x}(\mathbf{x}) + \phi_3 \frac{\partial^3 c}{\partial x^3}(\mathbf{x}) + \phi_3 \frac{\partial^3 c}{\partial x \partial y^2}(\mathbf{x}) \\ \phi_1 \frac{\partial c}{\partial y}(\mathbf{x}) + \phi_3 \frac{\partial^3 c}{\partial y^3}(\mathbf{x}) + \phi_3 \frac{\partial^3 c}{\partial x^2 \partial y}(\mathbf{x}) \end{bmatrix}$$

The polymers are very small (on a macroscopic scale) so we can assume that viscosity is much more important than elasticity in this system. So we can say that any velocity a polymer has is a direct consequence of the force felt by that polymer at that time. So

$$\mathbf{F} = \mu \mathbf{v}$$

where μ is a viscosity factor and \mathbf{v} is the polymer's velocity vector. So we can now relate the velocity vector field due to entanglement to the concentration surface.

Overall PDE. We can use conservation of solute for our overall PDE. This equation is

$$\frac{\partial c}{\partial t} + \nabla \cdot (\mathbf{v}c) = 0$$

First, let's enter entanglement into the equation:

$$\mathbf{v} = \frac{\mathbf{F}}{\mu}$$

and thus

$$(1) \quad c_t + \left(\frac{\phi_1}{\mu} cc_x + \frac{\phi_3}{\mu} cc_{xx} + \frac{\phi_3}{\mu} cc_{xy} \right)_x + \left(\frac{\phi_1}{\mu} cc_y + \frac{\phi_3}{\mu} cc_{yy} + \frac{\phi_3}{\mu} cc_{xy} \right)_y = 0$$

For simplicity, let's define a new variable

$$g \equiv \frac{\phi_1}{\mu} c + \frac{\phi_3}{\mu} \nabla^2 c$$

Substituting this into Equation 1 we get

$$c_t + (cg_x)_x + (cg_y)_y = 0$$

Let's introduce new variables to account for surface tension:

$$\begin{aligned} \alpha &\equiv \frac{\phi_3}{\mu} \\ \gamma &\equiv \frac{\phi_1}{\mu} - k_{\text{surface tension}} \end{aligned}$$

Adding the other effects, we get our PDE system:

$$(2) \quad \begin{aligned} g &= \gamma c + \alpha \nabla^2 c \\ c_t + e^{-\beta t} \left((cg_x)_x + (cg_y)_y \right) &= e^{-\beta t} D \nabla^2 c \end{aligned}$$

Force Function. Equation 2 needs the coefficients α and γ to be used. As shown above, these coefficients require a function f that represents the force felt by a polymer due to another polymer a distance x away. Let's treat each polymer as a non-hookean spring. So one side of each is tethered to the water, while the other is some random length away, at some random angle, as shown in Figure 4. The effective length of each spring (E_1, E_2) is the distance from the base to the intersection of the springs. Through some simple geometry we get

$$\begin{aligned} E_1 &= x \frac{\sin \theta_2}{\sin(\theta_1 + \theta_2)} \\ E_2 &= x \frac{\sin \theta_1}{\sin(\theta_1 + \theta_2)} \end{aligned}$$

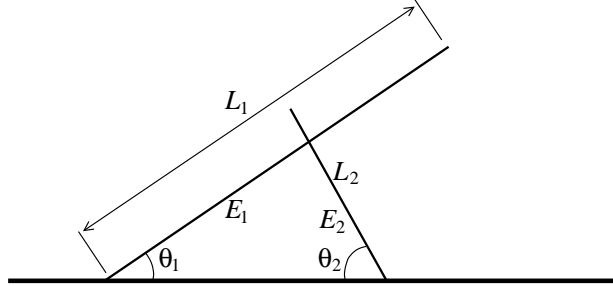


FIGURE 4. This is a diagram showing the two entropic springs with lengths L_1, L_2 , effective lengths E_1, E_2 and angles θ_1, θ_2 .

If the springs exert forces F_1 and F_2 then the 2D force felt by the base of one of the springs is

$$(3) \quad F_{\text{binary}} = \frac{\cos(\theta_1 + \theta_2)}{2} (F_1 \cos \theta_2 + F_2 \cos \theta_1)$$

According to [1, Page 697], the entropic restoring force of a polymer spring is

$$(4) \quad F_{\text{spring}} = \frac{kT}{2l} \ln \left(\frac{1 + \nu}{1 - \nu} \right)$$

where k is Boltzmann's constant, T is the temperature, l is the length of a single monomer and $\nu = \frac{n}{N}$ is the extension from the rest state of the spring when the polymer is stretched or compressed by nl and N is the number of monomers in the chain. The rest length of an entropic spring is $l\sqrt{N}$ if $N \gg 1$. So Equation 4 can be rewritten as

$$F_{\text{spring}} = \frac{kT}{2l} \ln \left(\frac{lN + L - l\sqrt{N}}{lN - L + l\sqrt{N}} \right)$$

The forces F_1 and F_2 in Equation 3 don't take into account the effective lengths of the spring. A good way to account for the effective lengths is to scale F_1 by $\frac{E_1}{L_1}$ and F_2 by $\frac{E_2}{L_2}$. Substituting into Equation 3 we get

$$(5) \quad F_{\text{binary}} = \frac{xkT}{8l \tan(\theta_1 + \theta_2)} \left(\frac{\sin(2\theta_2)}{L_1} \ln \left(\frac{lN + L - l\sqrt{N}}{lN - L + l\sqrt{N}} \right) + \frac{\sin(2\theta_1)}{L_2} \ln \left(\frac{lN + L - l\sqrt{N}}{lN - L + l\sqrt{N}} \right) \right)$$

To get the force function $f(x)$ the expected value of F_{binary} is obtained. So

$$(6) \quad f(x) = E(F_{\text{binary}})$$

$$(7) \quad = \int \int \int \int F_{\text{binary}} P(\theta_1) P(\theta_2) P(L_1) P(L_2) dL_2 dL_1 d\theta_2 d\theta_1$$

Let's assume a uniform distribution of θ above the water so $P(\theta_1) = P(\theta_2) = \frac{1}{\pi}$. Now we need a distribution for the length of the entropic spring. This is derived in [5, Page 267] by analyzing random walks as

$$P(L) = 4\pi L^2 \left(\frac{3}{2\pi Nl^2} \right)^{\frac{3}{2}} e^{-\frac{3L^2}{2Nl^2}}$$

The only thing left before integrating to find $f(x)$ is to set $F_{\text{binary}} = 0$ if either of the polymers are pointing away from each other or if they're too far. When this is done, the integral can be computed to produce $f(x)$.

EQUATION ANALYSIS

Let's look at the one-dimensional steady-state version of Equation 2:

$$g = \gamma c + \alpha c_{xx}$$

$$(cg_x)_x = Dc_{xx}$$

If we ignore diffusion we get $K = \gamma c + \alpha c_{xx}$ which implies a sinusoidal solution with a period of $2\pi\sqrt{\frac{\alpha}{\gamma}}$. So each bump in the solution will be $\pi\sqrt{\frac{\alpha}{\gamma}}$ wide. This is very good because experimentally, we know that dots have a length scale and are not randomly sized.

Now let's look at the sign of c in Equation 2. If c is positive at some point in time then, by the intermediate value theorem, in order for it to become negative, it will have to go through $c = 0$. If $c = 0$ then $c_t = D\nabla^2 c$. Since some point will reach $c = 0$ first, we can assume that $c > 0$ is true all around it. Thus $\nabla^2 c > 0$ is true for the point where $c = 0$. This means that $c_t > 0$ is true there too. So if any point reaches $c = 0$, it will move back to the positive side. So, analytically, at least, $c \geq 0$ will be true everywhere if the initial conditions are positive.

FITTING THE EXPERIMENTAL PARAMETERS

There are several variables that can be adjusted in the deposition process. These include the polymer used, the solvent used, the temperature of the solution and the water, initial concentration of the solution, and various parameters relating to the compression in the Langmuir-Blodgett trough. According to [2], the compression parameters do not affect the type of features observed, just their relative size. So we are not interested in those. Thus the experimental parameters we care about (and their values for a particular experiment) are

Polymer type	51k PS-PEO: $N_{\text{PEO}} = 82$, $N_{\text{PS}} = 459$, $l_{\text{PS}} = 1.8\text{\AA}$
Solvent type	Chloroform
Temperature	25°C
Concentration	1.0 $\frac{\text{mg}}{\text{mL}}$

The system parameters in the model are α , β , γ , D , μ , $k_{\text{surface tension}}$, N and l . So far, I have not found a way to determine β and $k_{\text{surface tension}}$, so for the time being, those are set to 0. N and l come directly from the polymer type (the PS part of it because that is the part that gets entangled). ϕ_1 and ϕ_3 come from the force function as described above. Combined with μ , we can use these to get α and γ . According to [4], the viscosity of liquid chloroform at 25°C is 0.537mPa·s. We need to multiply this by a length scale of our polymer to get μ . An appropriate length scale is the 2 times the radius of gyration of the polymer. According to [2], $\sqrt{\langle R_g^2 \rangle} = 7.12\text{nm}$. So $\mu = 7.65 \times 10^{-12} \frac{\text{N}}{\text{s}}$. According to a numerical evaluation (described below), $\phi_1 = 0.05\text{Nm}$ and $\phi_3 = 5.6 \times 10^{-19}\text{Nm}^3$. Thus $\alpha = 7.3 \times 10^{-8} \frac{\text{m}^4}{\text{s}}$ and $\gamma = 6.5 \times 10^9 \frac{\text{m}^2}{\text{s}}$. So we can now compute the width of the dots generated with these parameters: $\pi\sqrt{\frac{\alpha}{\gamma}} \approx 10\text{nm}$. According to [2], the dots are about 100nm wide. So the estimate is off by a factor of 10. This could be because the

surface tension contributes negatively to γ and would make it smaller which would enlarge the estimate. The diffusion coefficient D can be obtained from Einstein's diffusion equation:

$$D = \frac{kT}{6\pi\eta R_g}$$

where k is Boltzmann's constant, T is the temperature, η is the viscosity in mPa·s and R_g is the radius of gyration. This produces $D = 5.7 \times 10^{-11} \frac{m}{s}$. Finally, the initial conditions of the simulation are defined completely by the concentration of the solution. The initial conditions used were a constant concentration across the simulation space with a small (1%) random disturbance. We have $1.0 \frac{mg}{mL} = \frac{10^3 N_A}{M_W} \frac{molecules}{m^3}$ where N_A is Avogadro's number and M_W is the molecular weight of the polymer. If we assume that the depth of the layer is $2\sqrt{\langle R_g^2 \rangle}$ then the initial concentration is $\frac{2\sqrt{\langle R_g^2 \rangle} 10^3 N_A}{M_W} \frac{molecules}{m^2} = 1.67 \times 10^{14} \frac{molecules}{m^2}$.

So for the specific problem described in the table above, the simulation parameters are:

α	$7.3 \times 10^{-8} \frac{m^4}{s}$
γ	$6.5 \times 10^9 \frac{m^2}{s}$
D	$5.7 \times 10^{-11} \frac{m}{s}$
μ	$7.65 \times 10^{-12} \frac{N}{m \cdot s}$
N	459 monomers
l	1.8 Å
Initial c	$1.67 \times 10^{14} \frac{molecules}{m^2}$

NUMERICS

Two separate numerical programs are required to run the simulations. The first computes the force function $f(x)$ from Equation 7. This is a simple numerical integrator written in C. After it runs, it produces $f(x)$ and the constants ϕ_1 and ϕ_3 can be extracted from that.

The second program is the numerical PDE solver to solve Equation 2. This C program uses finite differences to find the solution. No-flux boundary conditions are used to conserve mass. The initial conditions are a constant concentration across the simulation space with a 1% random disturbance added. Further, since the values of c were very large when fit to experimental parameters, a normalized c was used. To accomplish this, a change of variables was made:

$$c = c_* \bar{c}$$

where c_* is the normalized concentration and \bar{c} is some constant concentration that serves as the scaling factor. When this is propagated through the equation we get

$$(8) \quad \begin{aligned} g &= \gamma c_* + \alpha \nabla^2 c_* \\ \frac{1}{\bar{c}} c_{*t} + e^{-\beta t} \left((c_* g_x)_x + (c_* g_y)_y \right) &= e^{-\beta t} D \nabla^2 c_* \end{aligned}$$

This can be seen as a change of variables for t . Let $s(t) = \bar{c}t$ so $\frac{\partial c_*}{\partial t} = \frac{\partial c_*}{\partial s} \frac{ds}{dt}$ which means that $\frac{1}{\bar{c}} c_{*t} = c_{*s}$.

The computations took relatively long periods of time so code efficiency was very important. Initially, the code was executed on Pentium 4 linux machines. Soon it became apparent that the performance of these Pentium 4 computers was inferior to that of Pentium 3 computers of much slower clock speed. This turned out to be true very consistently so it is definitely not a configuration issue. In an attempt to make the Pentium 4 computers to run as fast as they reasonably should, gcc 3.1.1 was used with the Pentium 4 optimizations turned on. This produced a small speed-up but not one that was enough to beat the Pentium 3 machines. Thus, until gcc is able to optimize Pentium 4 code well, there is no reason to use these computers instead of the slower clock speed, but faster computationally Pentium 3s.

RESULTS

First, a force function $f(x)$ had to be generated. This was done for the 51k polymer described above. This plot is different from the sketch in Figure 2 in that the force does not go to infinity for small separations. This is because when computing the force function, the PEO pancakes were not taken into account and thus

this great repulsive force does not exist. Since throughout the model we assume that the pancakes never come into contact and thus never subduct, the difference is not important.

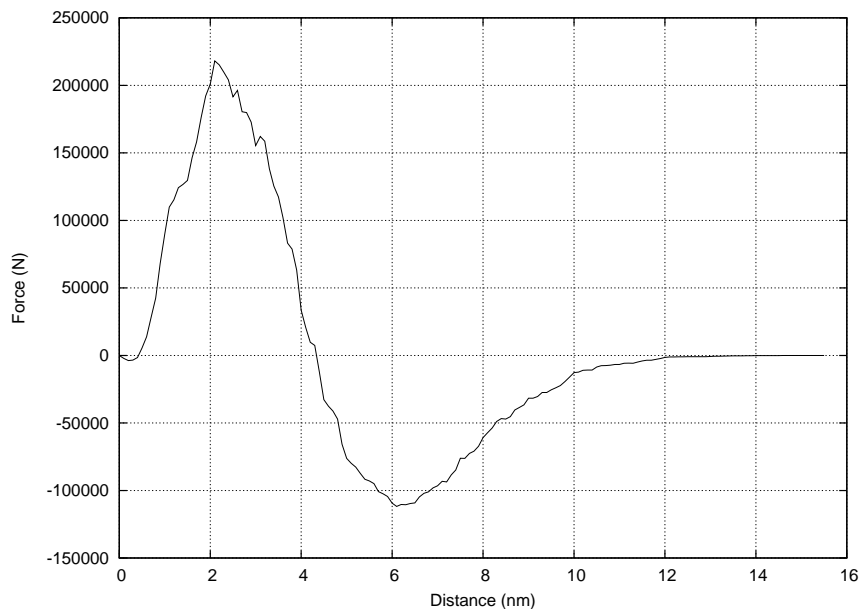


FIGURE 5. This is the force function $f(x)$ that describes the binary interaction of two 51k polymers.

Equation 8 was tested with arbitrary parameters to make sure that it was capable of producing the behavior demonstrated by the physical system (dots, spaghetti, continents). The simulation produced plots shown in Figure 6. An earlier time step is on the left. There we can see a continuous piece of spaghetti in the top-right corner. After some time has passed, however, that spaghetti starts breaking up into two separate dots, as shown in a later point in time on the right. So dots form from spaghetti and spaghetti remains only if the system has annealed before it had a chance to break up. Results using real data are upcoming.

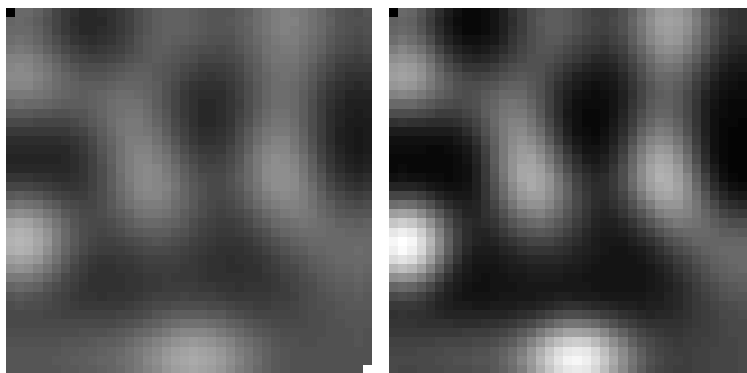


FIGURE 6. These are two snapshots of a simulation that show the development of dots from spaghetti.

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