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Double Gyroid Morphology of the Diblock Copolymer Problem

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Like oil and vinegar, material science and mathematics may be incompatible, but a variety of incompatible fields, in the presence of computer simulations and graphics as surfactants, can self-assemble into a rich variety of meso-fields.

Microphase separation is driven by chemical incompatibilities between the different blocks that make up block copolymer molecules. In the diblock copolymer melt, the final equilibrium state then tends to be periodic structures such as lamellar, column, spherical and bicontinuous cubic meso-phases. Why do such morphologies occur in the mixtures? One can guess this along the following lines: the dominant factor in the determination of the morphology is the area-minimization of the interface region, whereas its enclosed region has a fixed volume. Surfaces that satisfy this mathematical condition are said to have constant mean curvature (CMC). The familiar triply periodic cubic geometries such as the primitive (P), diamond (D) and gyroid (G) surfaces form a representative class of CMC surfaces. It is also reasonable that the interface should be periodic at a molecular length scale (10 ~ 100 nm).[5, 13]

Why can we observe only the G-surface family as the cubic phase in experiments? Furthermore, it is splendid that they form the double-network structures of the Ia $\bar{3}$ d-symmetry. Space groups are usually different for double- and single-network systems even though they are based on the same minimal surface because the latter has lower symmetry than the former. Note that the G has the I4 $_1$ 32-symmetry which means the 3-screw axis tunnels. In this short note, we would like to demonstrate the mechanism behind the appearance of the double gyroid (DG) phase on the basis of the most essential aspects of copolymers.

Energy Minimizers of Diblock Copolymer Problem and Simulation

We deal with the gradient system with nonlocal effects and focus on the characterization of unit cell of the DG morphology in this study.[12] By minimizing the free-energy functional $F_{\epsilon,\sigma}(= E_1 + E_2 + E_3)$ following the Cahn-Hilliard-Oono equations,[1] we are looking for the equilibrium state of order $O(1)$, i.e., it has a periodic structure in space with Ω being its unit domain. Notation Ω represents the physical space.

$$F_{\epsilon,\sigma}(u) = \int_{\Omega} \left(\frac{\epsilon^2}{2} |\nabla u|^2 + W(u) + \frac{\sigma}{2} |(-\Delta)^{-1/2}(u - \bar{u})|^2 \right) dr, \quad (1)$$

where $\bar{u} = |\Omega|^{-1} \int_{\Omega} u dr$ and $(-\Delta)^{-1/2}$ is a fractional power of the Laplace operator. The phase function u describes roughly the microscopic state of the polymers relevant to its

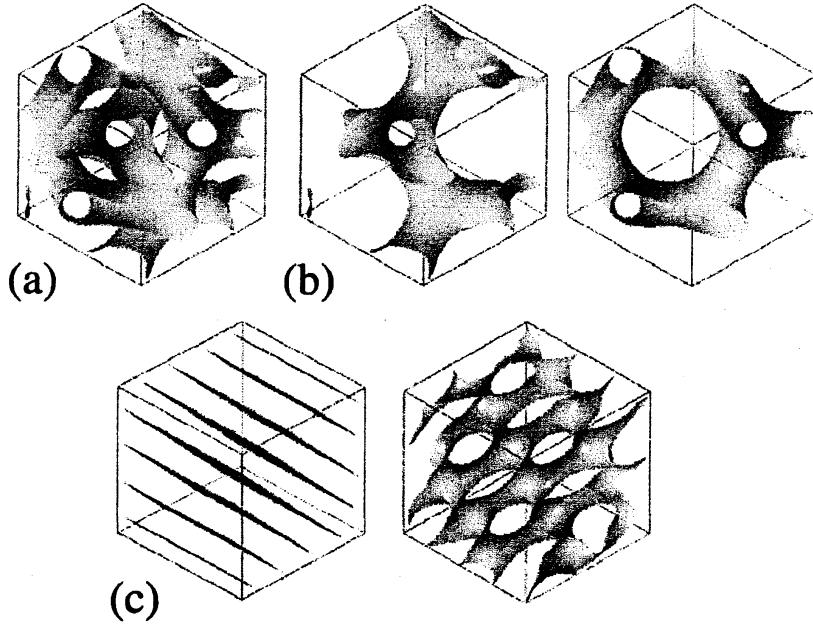


Figure 1: The views of isosurfaces at $\bar{u} = 0.10$ from the $[111]$ -directions; (a) Double gyroid (DG) and (b) a pair of gyroid single-network forms a chiral-network. (c) Lamellar (L, the layer interval is $2^{-3/2}$) and Ortho-rhombohedral (OR).

transition between phases. The function $W(u)$ is set to the form $(u^2 - 1)^2/4$, reflecting the segregation of monomers over mixtures. The functional (1) was introduced essentially by Ohta and Kawasaki.[10] The first term minimize unfavorable interfaces and the third term avoid over-stretching the copolymer blocks. The period of the minimizer is a meso-scale between which results from compromising between these opposite tendencies.

Nishiura and Ohnishi reformulated the mathematical basis of the Ohta-Kawasaki model and they formally concluded that there exists a unique scaling, the characteristic domain size of morphology is proportional to $(\epsilon/\sigma)^{1/3}$, and the energy of the system is scaled as $\epsilon^{2/3}\sigma^{1/3}$ for the one-space dimension.[7, 9] The parameter ϵ and σ is proportional to the interfacial thickness at the bonding point and to the inverse of the square root of the total chain length, respectively. Choksi and Ren rederive the functional of (1) by using self-consistent mean field theory, connecting those phenomenological parameters to the microscopic material parameters.[3]

In the approach to $\epsilon \rightarrow 0$, the significant contributions to $F_{\epsilon,\sigma}$ tend to come equally from all three terms of order $O(\epsilon)$. Assuming the sharp interface interpolation for the stacked layers, we can replace $\epsilon^2 \int_{\Omega} |\nabla u|^2 dr/2 + \int_{\Omega} W(u) dr$ by $\epsilon \int_{\Omega} |\nabla u| dr$. As a result, the $E_1 + E_2$ correspond to about ϵ times the total area of the interface region of $O(1)$. Ren and Wei proved that the Γ limit of a rescaled functional $F_{\epsilon,\sigma}/\epsilon$ for the ν -mode layer solution in $\Omega = [0 : 1]$ can be written by[11]

$$\frac{F_{\epsilon,\sigma}(\nu)}{\epsilon} = \left[c\nu + \frac{(1 - \bar{u}^2)^2}{24\nu^2} \left(\frac{\sigma}{\epsilon} \right) \right], \quad (2)$$

where $c = \int_{-1}^1 \sqrt{2W(u)} du$. By the variation of (2) with respect to ν in $\Omega = [0 : 1]$, the 2-mode

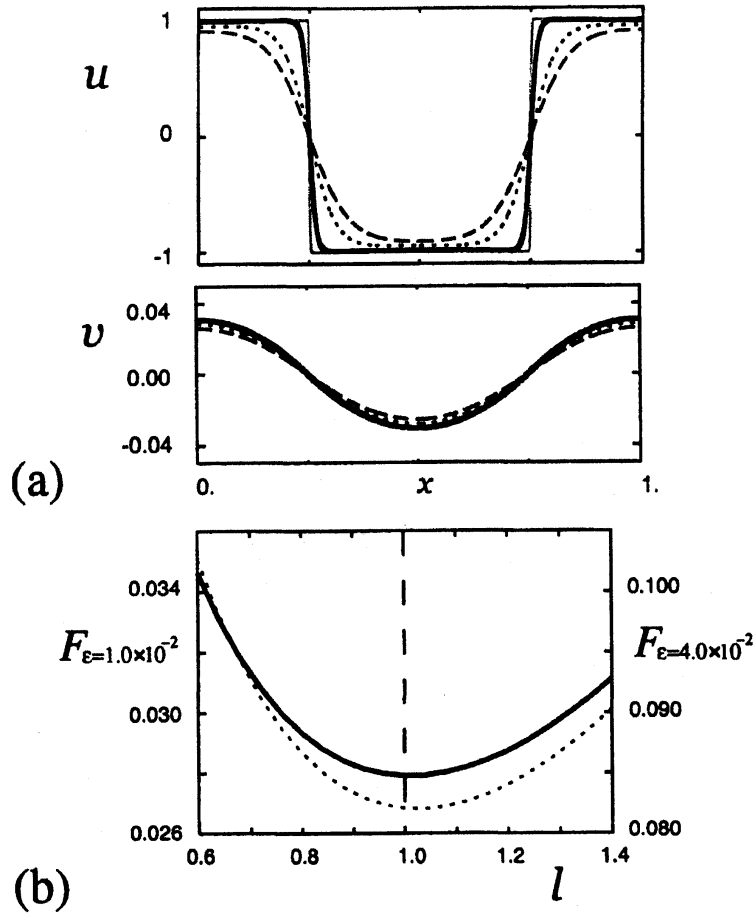


Figure 2: (a) The ϵ -dependence of profiles of the one-dimensional minimizer. The chemical potential v satisfies $-v_{xx} = u - \bar{u}$, $v_x(0) = v_x(1) = 0$ and $\int_0^1 v dx = 0$. The ϵ are chosen as follows; broken: 6.0×10^{-2} , dotted: 4.0×10^{-2} , solid: 1.0×10^{-2} , gray: 1.0×10^{-3} . (b) The minimization of $F_{\epsilon, \sigma}$ with respect to l when $\sigma/\epsilon = 2^{13/2}(1 - \bar{u}^2)^{-2}$. The ϵ are chosen as follows; solid: 1.0×10^{-2} , dotted: 4.0×10^{-2} .

type solution is characterized as the global minimizer if the ratio of $\sigma/\epsilon = 2^{13/2}(1 - \bar{u}^2)^{-2}$. Each term of $F_{\epsilon, \sigma}$ therefore becomes equally balanced as $F_{\epsilon, \sigma}(2)/\epsilon = 4\sqrt{2}/3 + 2\sqrt{2}/3 = 2\sqrt{2}$. This is verified numerically by computing the $F_{\epsilon, \sigma}$ value as $(E_1, E_2, E_3) = (9.44 \times 10^{-3}, 9.41 \times 10^{-3}, 9.41 \times 10^{-3})$ for $(\epsilon, \bar{u}) = (1.0 \times 10^{-3}, 0.00)$. Figure 2 shows the graph of $F_{\epsilon, \sigma}$ value for the 2-mode type minimizers which the layer interval is l ($\Omega = [0 : l]$). For small ϵ , the global minimizer is obtained if $l = 1$, while the optimal system size l becomes slightly larger than unity for large ϵ .

Hereafter, $\Omega \subset \mathbb{R}^3$ is taken to be the cube $(0 : l]^3$ subject to the periodic boundary condition. In order to realize the one unit of triply periodic cubic geometry, we loose apply the ratio of $\sigma/\epsilon = 2^{11}(1 - \bar{u}^2)^{-2}$, in which the L structure (the layer interval is $2^{-3/2}l$) gives the period of the global minimizer in $\epsilon \rightarrow 0$. This validation depends on whether the three-dimensional structures organize observable phenomena, not on whether or not the theory was used correctly from a mathematical standpoint. Nevertheless, the theoretical result

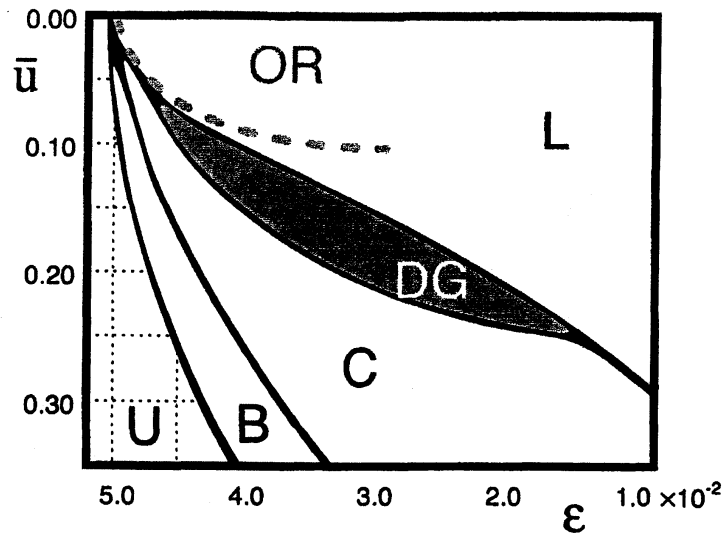


Figure 3: The $\bar{u}$ - ϵ phase diagram of the stable morphology, including the hexagonal columns (C), body-centered cubic spheres (B) and uniform state (U), when $\sigma/\epsilon = 2^{11}(1-\bar{u}^2)^{-2}$. The broken gray line shows the border between the DG-OR phases. In approaching $\bar{u} = 0.00$, the $F_{\epsilon,\sigma}$ value of OR becomes smaller than that of DG.

described above leads us to reflect the DG morphology in the gradient system of (1).

By minimizing $F_{\epsilon,\sigma}$ from the initial uniform state $u = \bar{u}$ perturbed randomly, the equilibrium morphologies illustrated in Fig.1 are dictated in the same parameter region of $(\epsilon, \bar{u})$. [12] In the limit of $\epsilon \searrow 0$, the contributions from each term of $F_{\epsilon,\sigma}$ are balanced in the order of $O(\epsilon)$ as $(E_1, E_2, E_3) = (2.60 \times 10^{-2}, 2.79 \times 10^{-2}, 2.35 \times 10^{-2})$ for the L phase, while $(2.39 \times 10^{-2}, 2.68 \times 10^{-2}, 2.89 \times 10^{-2})$ for the DG phase when $(\epsilon, \bar{u}) = (1.0 \times 10^{-2}, 0.10)$. The ratio between each term in $F_{\epsilon,\sigma}$ reflects the geometrical property of the minimizer.

Figure 3 illustrates the phase diagram obtained numerically from the comparison of the $F_{\epsilon,\sigma}$ between the candidate structures. We compare here the $F_{\epsilon,\sigma}$ values with changing l slightly in order to select the layer spacing makes the lowest-energy state. The L phase is stable for small ϵ , whereas the DG phase is stable for intermediate range of ϵ . The small ϵ regime of the phase diagram between the L and C phases has been confirmed experimentally with the morphology phase behaviors of ternary ($C_{16}E_7/D_2O/C_{12}H_{26}$) mixtures. [6] The local phase behavior obtained from the skeleton model of (1) investigated here can be applied to describe roughly a variety of meso-phase behaviors observed by experiment.

Some Geometrical Properties of Gyroid Minimizers and Discussion

We investigate here some measures of the level set $\Gamma \equiv \{r \in \Omega : u(r) = \bar{u}\}$ obtained in the previous section. As shown in Table I, a border whether the area Γ of the OR morphology is smaller than that of DG falls in the region around $\bar{u} = 0.10$ for $\epsilon = 4.0 \times 10^{-2}$. This is consistent with the DG-OR border line of Fig.3. The local mean curvatures for $\epsilon = 4.0 \times 10^{-2}$ distribute around the zero value rather sharply than that for $\epsilon = 1.0 \times 10^{-2}$. When $\bar{u} = 0.00$, in particular, the mean curvature of the interface Γ of OR approaches into the zero value,

Table 1: The $\bar{u}$ -dependence of Area Γ and integral of mean curvature ($\int_{\Gamma} H dS$) over the DG-OR transition region

$\bar{u}$	Area Γ				$\int_{\Gamma} H dS$			
	$\epsilon = 1.0 \times 10^{-2}$		$\epsilon = 4.0 \times 10^{-2}$		$\epsilon = 1.0 \times 10^{-2}$		$\epsilon = 4.0 \times 10^{-2}$	
	DG	OR	DG	OR	DG	OR	DG	OR
0.00	5.570	5.336	5.353	5.293	8.581	3.331	9.878	0.197
0.05	5.497	5.308	5.306	5.270	9.310	4.371	10.097	4.821
0.08	5.450	5.287	5.275	5.257	9.687	4.934	10.298	5.795
0.09	5.435	5.279	5.261	5.253	9.814	5.124	10.178	6.075
0.10	5.420	5.272	5.250	5.248	9.944	5.314	10.238	6.326
0.11	5.405	5.264	5.239	5.242	10.075	5.477	10.301	6.558
0.12	5.389	5.256	5.228	5.237	10.258	5.675	10.367	6.774
0.15	5.339	5.230	5.192	5.219	10.731	6.255	10.570	7.534
0.20	5.249	5.182	5.128	5.188	11.326	7.220	10.916	8.792

while that of DG is 1.84. When ϵ is large, in addition, the interfacial energy $E_1 + E_2$ dominates the total energy $F_{\epsilon,\sigma}$. [12] The interface Γ of our system therefore can be well approximated by DG with CMC.

It is worth noting the some geometrical measures of the OR morphology. In ref.[6] we used the symbol "R" instead of OR, however OR may be appropriate for the orthorhombic form of the Fddd symmetry.[2] We estimate that 80% of the total surface has zero or negative Gaussian curvature K for $\epsilon = 4.0 \times 10^{-2}$ (67% for $\epsilon = 1.0 \times 10^{-2}$). The interface Γ of OR, in other words, has saddle-shaped areas everywhere. The unit cell investigated here is depicted in Fig.1. The Euler characteristic $\chi \equiv (2\pi)^{-1} \int_{\Gamma} K dS$ is -24 , while that of DG is $-16 (= -8 \times 2)$. In this connection, each single-network of DG shown in Fig.1 (b) has a volume fraction of 22.5%, area Γ of 2.63 and mean curvature of about 1.94, while the area Γ of 2-period G is 6.24 and the mean curvature is nearly zero when $(\epsilon, \bar{u}) = (4.0 \times 10^{-2}, 0.10)$. Our results of Table I indicates the existence of an $\bar{u}$ -family of OR surfaces. Those objects play a role of intermediate state and should be responsible for the transition between L and DG phases.[6, 8] It is desirable to probe the existence of a OR-surface with CMC.

Now we try to explain why the G-surfaces are chosen as the global minimizer and they form the double-network of the Ia $\bar{3}$ d-symmetry. In the rest of this note, we suppose the following CMC system that the equilibrium morphology should be determined by the interface area-minimization, in which the period of global minimizer has the value of $2^{-3/2}$ in a cube. This makes sense because the covalent linkages between different blocks of a molecule serves to limit the phase separation to a characteristic scale length. Under this condition, we compare the area of CMC G-, P- and D-surfaces with $2^{5/2}$ of stacked layers.

The first step is to make 2-period CMC surfaces (a volume fraction of 50%) in a cube. According to the data of CMC surfaces,[4] the $area(G)$ is $6.18 (= 3.09 \times 2)$ and the $area(P)$ and $area(D)$ is $6.65 (\approx 2.35 \times 2^{3/2})$ and 7.68 , respectively. The area of G is the smallest among the 2-period cubic surfaces, but it is still larger than that of L. Second, we consider a period of double-network CMC surfaces (double of a volume fraction of 25%). The $area(DG)$ is $5.46 (= 2.73 \times 2)$, while $area(DP)$ and $area(DD)$ is $5.66 (\approx 2.00 \times 2^{3/2})$ and 6.72 . Notations DP and DD represent double primitive and double diamond, respectively. It is shown that

the DG morphology only has smaller interface area smaller than stacked layers, i.e., the inequality between areas is expressed by $area(DG) < area(L) < area(G)$. Accordingly, we argue that, in the presence of the characteristic layer spacing, the interface area per unit cube can be made smaller than that of the lamellar morphology when a pair of gyroid surfaces forms a double-network.

Our argument may be no more than a revival of the conventional physics based on the balance of the interfacial energy and configurational entropy. Nevertheless, it provides us with a useful intuitive basis for understanding the mechanism behind the appearance of DG phase in terms of "large and small" among some geometrical measures. Overall, we demonstrate that the gradient system with nonlocal effects is successful in reflecting the double gyroid phase observed in experiment and focus on the characterization of this intricate interconnected triply periodic self-assembled network morphology.

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