Nearly continuous transitions to periodic structures in block copolymer melts

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ABSTRACT. We analyze nearly continuous transitions to periodic structures expanding the density of the periodic structure in multiple harmonics. A three dimensional hexagonal structure identified as a “Lamellar-Catenoid” is the equilibrium structure near the transition. It consists of alternating lamellar domains connected by an orthogonal array of hexagonally packed cylinders. We obtain the periodicity, the density distribution inside the unit cell and the equilibrium morphology for diblock copolymers melts of various molecular compositions.

RESUMEN. Analizamos transiciones a estructuras periódicas expandiendo la densidad de la estructura en armónicos. La estructura de equilibrio encontrada es una lamela-catenoide, una estructura hexagonal en tres dimensiones. Consiste en dominios lamelares conectados ortogonalmente por cilindros formando un arreglo hexagonal. Obtenemos la periodicidad, la densidad en la celda unitaria y la morfología de equilibrio en bi-copolímeros de varias composiciones moleculares.

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The possibility of nearly continuous transitions from an isotropic state to a periodic structure has led to numerous studies of the equilibrium structure at the transition point in systems ranging from weak crystallization in liquids \[1-4\] to self-assembly systems, such as block copolymers \[5-8\]. The conventional Landau mean field approach \[1,2\] (LMFA) predicts a bcc structure. When the density fluctuations are self-consistently included in the analysis \[4\] a lamellar structure is obtained. By expanding the density in the periodic structure in multiple harmonics, we show here that a three dimensional hexagonal structure is more favorable. In block copolymers, this structure is identified as a “lamellar-catenoid” \[8\]; it consists of alternating lamellar domains connected by an orthogonal array of hexagonally packed cylinders.

The transition is analyzed expanding the free energy of the isotropic state in power series of the density fluctuations \(\delta \rho(r)\) around the mean density \(\rho_0\) \[1\];

\[
\frac{\Delta F(\rho_k)}{kT} = \frac{1}{2!} \sum \rho_k \frac{\rho_{-k}}{S_0(k)} + \frac{1}{V^3!} \sum \Gamma_3(k, k', k'') \rho_k \rho_{k'} \rho_{k''} \delta(k + k' + k'')
\]

\[
+ \frac{1}{V^4!} \sum \Gamma_4(k, k', k'', k''') \rho_k \rho_{k'} \rho_{k''} \rho_{k'''} \delta(k + k' + k'' + k''')
\] (1)
where $\rho_k$ are the Fourier components of $\delta \rho(r)$. In most systems $S_0^{-1}(\{k\})$ has a minimum at a single wavevector magnitude $k^*$. In the LMFA, a continuous transition occurs at $T_c$ when the symmetry is such that $\Gamma_3 = 0$. At $T_c$, $S_0(|k| = k^*)$ diverges leading to an instability of the isotropic state to density fluctuations of wavevector magnitude equal to $k^*$.

At the transition $\delta \rho$ has the symmetry of the periodic structure. It can therefore be expanded in plane waves whose vectors are the reciprocal lattice vectors of the periodic structure, the compositional harmonics [1]. The largest contribution to the free energy in nearly continuous transitions ($\Gamma_3 \sim 0$) is from the first harmonic vectors [2] $|K_r^{(i)}| = k^*$, $r = 1, \ldots, n_1$, where $n_1$ is the number of nearest-neighbors (n.n.) in the reciprocal lattice; $n_1 = 1$ for a lamellar (lam), $n_1 = 3$ for hexagonally packed cylinders (hpc), $n_1 = 6$ for a bcc, etc. The distance between n.n. planes in the structure is $d = 2\pi/k^*$. Since higher harmonic vectors ($i > 1$) have larger magnitudes $|K_r^{(i)}| = \alpha_i k^*$, $r = 1, \ldots, n_1$, with $\alpha_i > 1$, their contribution is often neglected.

There are structures, however, whose first and second harmonic vectors have equal magnitudes. Consider a hexagonal (hex/$c/a$) structure with indices $(hkl\ell)$, $\ell = 2n$ [$i = -(h+k)$], and distance between planes $d(hk\ell) = \{(h^2+k^2+hk)/3a^2 + (c^2/\ell^2)\}^{-1/2}$, where $a$ is the lattice spacing in the hexagonal plane, and $c$ is the length of the perpendicular axis. The first harmonic vectors are $\{K_r^{(1)}\}_r=1,2,3 = \{(1010), (0110), (1\bar{1}00)\}$, and the second is $K_r^{(2)} = (0002)$. In a hexagonal structure the ratio $c/a$ is not fixed. In a close-packed structure $c/a = \sqrt{8/3}$ and $K_r^{(2)} = 1.0607k^*$. When $c/a = \sqrt{3}$, however, $|K_r^{(1)}| = |K_r^{(2)}| = k^*$. To analyze the hex/$c/a$ structure, higher order harmonics have to be considered in $\delta \rho$.

We expanded $\delta \rho$ up to the $m$-th harmonic for which $|K_r^{(m)}| = 2k^*$ for various structures (for $\Gamma_3 \sim 0$ the higher order harmonics $i > m$ are negligible near the transition),

$$\delta \rho(r) = \sum_{i=1}^m a_i \sum_{r=1}^{n_i} \{\exp[i(rK_r^{(i)} + \varphi_r^{(i)})] + \text{c.c.} \} $$

The lam structure, for example, is described by one dimensional vectors of magnitude $|K_r^{(i)}| = ik^*$ ($n_i = 1$), so $\alpha_i = i$ ($m = 2$). The vectors $\{K_r^{(i)}\}$, denoted by $\{i'\}$, for a two dimensional array of hexagonally packed cylinders (hpc) are shown in Fig. 1. For this morphology $n_1 = n_2 = n_3 = 3$ with $\alpha_1 = 1, \alpha_2 = \sqrt{3}$ and $\alpha_3 = 2$ ($m = 3$) and $k^*/2\pi = 2a/\sqrt{3}$ (where $a$ is the lattice spacing). The harmonic vectors of various three dimensional structures and their values of $n_i$ and $\alpha_i$ are listed in Table I.

Replacing the wavevector summations in (1) by sums over the allowed vectors in (2) one obtains

$$\Delta F = \frac{m \sum_{i=1}^m n_i S_0^{-1}(\alpha_i k^*)a_i^2 + \sum_{ijk} (\Gamma_3)_{ijk} \frac{a_i a_j a_k}{3!} + \sum_{ijkl} (\Gamma_4)_{ijkl} \frac{a_i a_j a_k a_l}{4!}}{k^*} $$

The $\delta(k + k' + k'')$ constraint in the third order term in (1) dictates that contributions to $(\Gamma_3)_{ijk}$ in (3) are possible only when the three vectors from the $i$-th, $j$-th and $k$-th harmonics add to zero; i.e., when three-vector circuits of the form $\pm K_r^{(i)} \pm K_r^{(j)} \pm K_r^{(k)} = 0$ are allowed in the structure. Similarly, to have a contribution $(\Gamma_4)_{ijkl} \neq 0$, four-vector circuits of the form $\pm K_r^{(i)} \pm K_r^{(j)} \pm K_r^{(k)} \pm K_r^{(l)} = 0$ are required.
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**Figure 1.** The hpc harmonic vectors \( \{ \mathbf{K}_r^{(i)} \} = \{ i \} \), \( r = 1, \ldots, n_i \), with \( n_i = 3 \) for \( i = 1, 2 \) and 3: \( \alpha_1 = 1, \alpha_2 = \sqrt{3} \) and \( \alpha_3 = 2 \) (\( m = 3 \)).

**Table 1.** Harmonic vectors for three dimensional periodic structures.

<table>
<thead>
<tr>
<th>( (hkil) )</th>
<th>( n_i )</th>
<th>( \alpha_i )</th>
<th>( (hk\ell) )</th>
<th>( n_i )</th>
<th>( \alpha_i )</th>
<th>( (hk\ell) )</th>
<th>( n_i )</th>
<th>( \alpha_i )</th>
<th>( (hk\ell) )</th>
<th>( n_i )</th>
<th>( \alpha_i )</th>
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<tr>
<td>(1010)</td>
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<td>(110)</td>
<td>6</td>
<td>1</td>
<td>(111)</td>
<td>4</td>
<td>1</td>
<td>(100)</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>(0002)</td>
<td>1</td>
<td>( \sqrt{3}/a )</td>
<td>(200)</td>
<td>3</td>
<td>( \sqrt{2} )</td>
<td>(200)</td>
<td>3</td>
<td>( \sqrt{4/3} )</td>
<td>(110)</td>
<td>6</td>
<td>( \sqrt{2} )</td>
</tr>
<tr>
<td>(1120)</td>
<td>3</td>
<td>( \sqrt{3} )</td>
<td>(211)</td>
<td>12</td>
<td>( \sqrt{3} )</td>
<td>(220)</td>
<td>6</td>
<td>( \sqrt{8/3} )</td>
<td>(111)</td>
<td>4</td>
<td>( \sqrt{3} )</td>
</tr>
<tr>
<td>(2020)</td>
<td>3</td>
<td>2</td>
<td>(220)</td>
<td>6</td>
<td>2</td>
<td>(311)</td>
<td>12</td>
<td>( \sqrt{11/3} )</td>
<td>(200)</td>
<td>3</td>
<td>2</td>
</tr>
</tbody>
</table>

For simplicity, let us first discuss a case when \( \Gamma_3 \) and \( \Gamma_4 \) in (1) are wavevector independent constants, and \( S_0^{-1}(|k|) = \tau + (|k| - k^*)^2 \) [3]. In this case \( (\Gamma_3)_{ijk} = A_{ijk} \Gamma_3 \) and \( (\Gamma_4)_{ijkl} = B_{ijkl} \Gamma_4 \) where \( A_{ijk} \) and \( B_{ijkl} \) are numerical factors evaluated counting the possible combinations of harmonic vectors that add to zero, weighted by the phase factors. For example, the term \( A_{111} \) for the hpc structure is evaluated counting the closed circuits formed with the \( \{ \mathbf{K}_r^{(i)} \}_{r=1,2,3} = \{ (1,0),(0,1),(1,1) \} \) vectors (see Fig. 1): there are six ways of arranging these vectors to sum to zero, plus six ways for their c.c., so \( A_{111} = 12 \cos(\varphi_1^{(1)} + \varphi_2^{(1)} + \varphi_3^{(1)}) \). On the other hand, counting the circuits of the form \( \pm K_1^{(1)} \pm K_2^{(1)} \pm K_3^{(1)} = 0 \) in the hpc, we obtain \( A_{112} = 12 \cos(\varphi_2^{(1)} - \varphi_1^{(1)} + \varphi_1^{(2)}) + 12 \cos(\varphi_3^{(1)} - \varphi_2^{(1)} + \varphi_2^{(2)}) + 12 \cos(\varphi_2^{(1)} - \varphi_3^{(1)} + \varphi_3^{(2)}) \), and so on. The terms \( B_{ijkl} \) are evaluated counting the four-vector circuits with their corresponding phase factors.

The resulting free energy (3) is minimized with respect to the phases \( \{ \varphi_r^{(i)} \} \). In centrosymmetric structures the phases are 0 or \( \pi \). This agrees with the phase minimization, since it leads to the largest or smallest possible \( A_{ijk} \) and \( B_{ijkl} \) values. Furthermore, the phases within a harmonic are all equal, \( \{ \varphi_r^{(i)} \} = \varphi_1 \) for \( r = 1, \ldots, n_i \). Therefore, only the phase shift between harmonics (or the "sign") needs to be determined.
We obtained the amplitudes that minimize the free energy \( \{a_i\} \), for a given set of \( \{\varphi_i\} \), \( i = 1, \ldots, m \), for each structure, and evaluated \( \Delta F(\{a_i\}, \{\varphi_i\})/kT \). Phase diagrams \( \tau/\Gamma_4 \) versus \( |\Gamma_3|/\Gamma_4 \) are constructed finding the structure with lowest \( \Delta F \). For all \( k^{*2}/\Gamma_4 > 0.05 \) the diagrams are almost identical. The phase shifts for the first three harmonics are \( \varphi_1 = \pi \) and \( \varphi_2 = \varphi_3 = 0 \) for the hpc and bcc, while \( \varphi_1 = \varphi_2 = \pi \) and \( \varphi_3 = 0 \) for the lam, square, hex\(_c/a\), simple cubic and fcc for \( \Gamma_3 > 0 \); all phases shift by \( \pi \) (opposite “sign”) when \( \Gamma_3 < 0 \). The coefficients \( A_{ijk} \) and \( B_{ijkl} \) for the first three harmonics for \( \Gamma_3 < 0 \) are given in Table 2. When \( |\Gamma_3|/\Gamma_4 = 0 \) the hex\(_\sqrt{3}\) has the lowest energy. As \( |\Gamma_3|/\Gamma_4 \) increases a bcc is obtained; transitions from bcc to hpc to hex\(_\sqrt{3}\) are observed as \( \tau \) decreases (transitions to fcc occur when \( k^{*2}/\Gamma_4 < 0.1 \)).

We now consider diblock copolymer melts which have unique morphological features. A net repulsive interaction between the A and B monomers (\( \chi > 0 \)) of the chemically linked A and B chains drives the system to segregate locally [5–8]. The degree of polymerization \( N \), the block copolymer composition \( f = N_A/N \), and the Flory interaction parameter \( \chi (\sim 1/T) \) determine the physical properties of the melt. When \( \chi N \) is small the block copolymer melt is isotropic. At \( \chi N = (\chi N)^r \), a transition to a periodic structure occurs, known as the microphase separation transition (MST). At the MST the copolymer blocks segregate into A-rich and B-rich domains that form periodic arrays termed microphases.

The observed morphologies are alternating lamellar domains (lam), hexagonally packed cylinders (hcp), body-centered cubic lattice of spheres (bcc), and bicontinuous double diamond nets (bdd) [9]. Near the transition, referred to as the weak segregation regime, a lamellar-catenaoid (lc) structure has been recently observed experimentally [8]. The lc is an array of lamellar domains connected perpendicularly by an array of hexagonally packed cylinders.

In incompressible block copolymer melts \( \delta \rho(r) \) is the local deviation of the concentration of A monomers from its mean value \( f \) [5]. The \( S_0^{-1}(k), \Gamma_3(\{k\}) \) and \( \Gamma_4(\{k\}) \) in (1) are functions of the bare two, three and four-monomer correlation functions \( G_{ij}, G_{ijk} \) and \( G_{ijkl}, (i,j,k,\ell = A,B) \) calculated by the random phase approximation method (RPA) [5–7]. In the RPA, \( S_0(k) \) in block copolymer melts is the scattering intensity in the disordered state [5]

\[
\frac{1}{S_0(k)} = \frac{Q(x)}{N} - 2\chi
\]  

where \( x = k^2 N \ell^2/6 \) and \( N \) is the number of segments of length \( \ell \) (for simplicity we assume here \( \ell_A = \ell_B \)) per chain. Since \( Q(x) \) has a minimum at \( x = x_0^* \), \( S_0(k) \) has a peak at \( k_0^* \) which is independent of \( \chi \). The peak position, a function of \( f \), scales as \( k_0^*(f) \sim 1/R_0 \), where \( R_0 \) is the unperturbed radius of gyration \( R_0 = (N/6)^{1/2} \ell \). For \( f = f_c = 0.5 \) (when \( \Gamma_3 = 0 \), \( S_0(|k| = k_0^*) \) diverges at \( (\chi N)c = Q(x_0^*(f_c))/2 = 10.495 \), leading to an instability of the isotropic state to density fluctuations of wavevector magnitude equal to \( k_0^* \). For diblock copolymer melts, the \( \Gamma_3(\{k\}) \) and \( \Gamma_4(\{k\}) \) in (1) are wavevector dependent functions defined in reference [5].

Leibler [5] evaluated the diblock copolymer free energy of various periodic morphologies keeping only the first harmonic vectors of the periodic structure. Since his analysis includes only the first harmonic, different space groups having the same first Bragg reflections are...
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Table II. Numerical factors $A_{ijk}$ and $B_{ijkl}$ for various periodic structures

<table>
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<th></th>
<th>Lam</th>
<th>hpc</th>
<th>hexc/a</th>
<th>bcc</th>
<th>fcc</th>
<th>simple cubic</th>
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<td>12</td>
<td>12</td>
<td>48</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$A_{222}$</td>
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<td>-12</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>48</td>
</tr>
<tr>
<td>$A_{333}$</td>
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<td>-12</td>
<td>-48</td>
<td>-48</td>
<td>0</td>
</tr>
<tr>
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<td>-72</td>
<td>72</td>
<td>72</td>
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<td>0</td>
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<td>144</td>
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<td>-144</td>
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<td>$B_{1111}$</td>
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<td>90</td>
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<td>$B_{2222}$</td>
<td>6</td>
<td>90</td>
<td>6</td>
<td>90</td>
<td>90</td>
<td>540</td>
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<td>$B_{3333}$</td>
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<td>90</td>
<td>90</td>
<td>2376</td>
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<td>216</td>
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<td>72</td>
<td>576</td>
<td>576</td>
<td>1152</td>
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<tr>
<td>$B_{1133}$</td>
<td>24</td>
<td>288</td>
<td>360</td>
<td>4752</td>
<td>1152</td>
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<td>288</td>
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<td>$B_{2222}$</td>
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<td>6</td>
<td>90</td>
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<td>540</td>
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<td>$B_{1122}$</td>
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<td>1296</td>
<td>1152</td>
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</table>

$(A_{122} = 0, B_{122} = 0$ and $B_{2222} = 0$ for all structures)

indistinguishable. For example, the first harmonic vectors that describe the bcc and the bdd structures are identical [7]. Similarly, the two dimensional hpc and the three dimensional hexc/a structures are indistinguishable. Because the single harmonic approximation does not discriminate between some of the observed microstructures, the higher harmonics must be included in the analysis.

Since in block copolymers the dependence of $\Gamma_3(K_{i_1}^{(s)}, K_{s}^{(j)}, K_{t}^{(s)})$ and $\Gamma_4(K_{i_1}^{(s)}, K_{s}^{(j)}, K_{t}^{(s)}, K_{u}^{(l)})$ on the angles between the harmonic vectors is very small [7], they can be approximated to functions of their magnitudes setting $\Gamma_3(\alpha_i k^*, \alpha_j k^*, \alpha_k k^*) = \Gamma_3([\alpha_i^2 + \alpha_j^2 + \alpha_k^2]/3)^{1/2} k^*$ and $\Gamma_4(\alpha_i k^*, \alpha_j k^*, \alpha_k k^*, \alpha_t k^*) = \Gamma_4([\alpha_i^2 + \alpha_j^2 + \alpha_k^2 + \alpha_t^2]/3)^{1/2} k^*$ where $\Gamma_3(k)$ and $\Gamma_4(k) = \Gamma_4(0, 0, k)$ are defined in reference [5] (both linear functions of $k^2$ for $|k| > k_0^*$ which slope increases as $f$ increases). With this simplification, $(\Gamma_3)_{ijk} = \Gamma_3([\alpha_i^2 + \alpha_j^2 + \alpha_k^2]/3)^{1/2} k^*) A_{ijk}$ and $(\Gamma_4)_{ijkl} = \Gamma_4([\alpha_i^2 + \alpha_j^2 + \alpha_k^2 + \alpha_l^2]/3)^{1/2} k^*) B_{ijkl}$ where $A_{ijk}$ and $B_{ijkl}$ are the numerical factors given in Table II. The scaling properties of $1/S_0(k)$, $\Gamma_3(k)$ and $\Gamma_4(k)$ dictate that $N\Delta F/KT$ in (3) is a function of $x^* = k^2 R_0^2$.

In the isotropic phase, away from the transition, $x^*$ is a constant $\chi$ and $N$ independent, so $k^* = k_0^*(f) \sim 1/R_0$. In the periodic structures the chains are perturbed [10]. A further minimization of (3) with respect to $k^2$ for each morphology is therefore required, giving
the periodicity $d = 2\pi/k^*$, as a function of $\chi$ and $N$ [6–7]. In Fig. 2 we plotted the LMFA phase diagram $f$ versus $\chi N$ after this minimization. Including the fluctuations self-consistently in the analysis [4], important for finite $N$ (or $k^* \neq 0$), we recently found hcp = hex$_{\sqrt{3}}$ structures for $N < 10^9$ [6]. Minimizing the $c/a$ ratio instead leads to hex$_{c/a}$ equilibrium structures even when $N \to \infty$ (fixing $c/a = \sqrt{8/3}$ leads to large chain stretching, $k^* \ll k^*_0$). the lam and the hpc previously found [3–8], are not present when the hex$_{\sqrt{3}}$ is considered.

In Fig. 3 we show the amplitudes $a_1$ and $a_2$ for the hex$_{\sqrt{3}}$ for $f = .5$ and .52 as a function of $\chi N$. For $f > .52$, $a_1/a_2 > 1$ at the transition, though as $\chi N$ increases $a_1/a_2 < 1$. The density distribution inside the unit cell is obtained from the values of $k^*$, $\{a_i\}$ and $\{\varphi_i\}$.
i = 1, \ldots, m. The hexc/a reconstructed in this way reveal that the hexc/a consists of lamellar domains connected by an orthogonal array of hexagonally packed cylinders rich in A, in a matrix rich in B. For the symmetric composition $f = .5$ the density rich in B has the same distribution as the density rich in A; i.e., the structure consist of lamellar domains of A perforated by cylinders of B alternated with lamellar domains of B perforated by cylinders of A, resembling the lamellar-catenoid structure observed by Thomas et al. [8]. The cylinders are hexagonally packed. When $f$ increases, however, the density distribution in the B rich (minority component) cylinders fades. Therefore, for larger $f$ the lamellar domains of A might not be perforated by cylinders (i.e., only the lamellar domains of the minority component are perforated by cylinders hexagonal packed). A similar "lamellar-catenoid" structure was recently found experimentally [11], though the packing arrangements of the cylinders perpendicular to the lamellar domains has not yet been determined experimentally.

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