Self-assembly of orthorhombic \textit{Fddd} network in simple one-component liquids

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Triply periodic continuous morphologies arising as a result of the microphase separation in block copolymer melts have so far never been observed self-assembled in systems of particles with spherically symmetric interaction. We report a molecular dynamics simulation of two simple one-component liquids which self-assemble upon cooling into equilibrium orthorhombic continuous network morphologies with the \textit{Fddd} space group symmetry reproducing the structure of those observed in block copolymers. The finding that the geometry of constituent molecules isn’t relevant for the formation of triply periodic networks indicates the generic nature of this class of phase transition.

The concept of microphase separation in fluids was introduced more than fifty years ago by Lebowitz and Penrose \cite{1}. They conjectured that amending the pair potential in the van der Waals model with an additional long-range repulsion can cause the macroscopic separation of liquid and gas phases in the spinodal domain to break into mesoscopic-scale patterns. In a separate development, it was suggested \cite{2} that fluids of immiscible macromolecules may form mesoscopic-scale structures composed of continuous percolating domains separated by minimal surfaces. Moreover, these microphases were conjectured to form morphologies with long-range translational order. These microphase transitions have been observed in block co-polymer melts producing a variety of multiply continuous periodic morphologies which are both elegant and remarkably useful \cite{3}. As a surprising discovery, the orthorhombic \textit{Fddd} network was observed \cite{4, 5}, the first non-cubic structure produced in soft-matter systems, raising the discussion about the origin of that symmetry breaking.

The self-assembly of the triply periodic networks in block copolymer melts is thought to be controlled by the minimisation of the inter-domain surface area and the conformation entropy of the molecular chains. Whether such a network can self-assemble in a system of particles with spherically symmetric interaction as a result of the liquid-gas microphase separation remains a question of both conceptual and practical interest. Landau theory and density-functional theory \cite{6, 7} predicted that triply periodic networks can be stabilised by the pair potentials with short-range attraction and long-range repulsion (SALR). The interparticle potentials in colloidal systems of spherical particles can be tuned to approximate those conjectured from the theoretical models \cite{8}. However, despite the extensive experimental efforts, triply periodic morphologies have never been observed in colloidal systems. \cite{9}.

Simulations using particles are indispensable for testing the ability of the theoretically conjectured SALR pair potentials to produce self-assembly of triply periodic networks. These networks, however, have so far never been observed self-assembling in simulations using the SALR pair potentials \cite{10–12}. Moreover, it was concluded, based on the density-functional calculations \cite{6}, that if one starts with a random particle configuration, such a system, due to the complexity of its free-energy landscape, wouldn’t be able to reach the minimum representing a triply periodic network. Thus, the conceptually significant question of whether a simple system of identical particles can self-assemble into a triply periodic network remains open.

This Letter reports a molecular-dynamics simulation of two different systems of identical particles with spherically-symmetric interaction which demonstrate microphase separation transitions upon cooling from a uniform liquid state. The phase diagrams for both systems are found to include domains of density and temperature where they self-assemble into equilibrium triply periodic morphologies possessing orthorhombic \textit{Fddd} space-group symmetry.

Each of the investigated molecular-dynamics models was composed of 16384 identical particles confined to a cubic box with periodic boundary conditions. They used two pair potentials, $V_1$ and $V_2$, shown in Fig.1. The potential energy for two particles separated by the distance $r$ is described by the functional form:

\begin{equation}
V(r) = a_1(r^{-m} - d)H(r, b_1, c_1) + a_2H(r, b_2, c_2) \quad (1)
\end{equation}

\begin{equation}
H(r, b, c) = \begin{cases} 
\exp \left( \frac{b}{r-c} \right) & r < c \\
0 & r \geq c 
\end{cases}
\end{equation}

The values of the parameters are presented in Table I. The reduced units used in this simulation are those used in the definition of the potentials.

This functional form of the pair potential is consistent with the general form of the SALR potentials and it was earlier found to produce columnar and lamellar
FIG. 1: Pair potentials used in this study. Solid line, $V_1$; dashed line, $V_2$.

| m | $a_1$ | $b_1$ | $c_1$ | $a_2$ | $b_2$ | $c_2$ | d |
|---|---|---|---|---|---|---|---|
| $V_1$ | 12 | 113 | 2.8 | 1.75 | 2.57 | 0.3 | 4.0 | 1.4 |
| $V_2$ | 12 | 113 | 2.8 | 1.75 | 2.57 | 0.3 | 3.1 | 1.4 |

TABLE I: Values of the parameters for the pair potentials.

FIG. 2: Phase diagrams of the simulated systems. Top and bottom, respectively, System I and System II. Open circles: isotropic liquid (ISO). Open squares: lamellar phase (LAM). Diamonds: $F_{ddd}$ phase. Crosses: columnar phase (COL).

FIG. 3: Left: Arrhenius plot for System II. Dots: isotropic liquid; squares: $F_{ddd}$ phase, cooling; open circles: $F_{ddd}$ phase, reheating. Right: an instantaneous particle configuration of the $F_{ddd}$ phase formed in System I.

transitions producing equilibrium periodic morphologies which were identified by visual inspection of the instantaneous particle configurations.

The density-temperature phase diagrams of the simulated systems are shown in Fig.2. Besides the domains of classical morphologies, lamellae and hexagonally packed cylinders, both systems exhibit domains where the microphase separation transitions produce equilibrium triply periodic networks with the $F_{ddd}$ space group symmetry. An instantaneous particle configuration of this microphase produced by System I is shown in Fig. 5. In the following we present a detailed analysis of the structure and the dynamical properties of the simulated $F_{ddd}$ morphologies.

For both systems the domains where the self-assembly of equilibrium $F_{ddd}$ microphase was observed extend within a significant range of densities. We also observe a difference in the systems’ phase behaviour. For System I, the $F_{ddd}$ domain is separated from the uniform liquid domain by a domain of lamellar phase. Therefore, it was only possible to produce the $F_{ddd}$ self-assembly by discontinuously quenching it from the equilibrium liquid state to a targeted range of temperatures, whereas System II performed the liquid-$F_{ddd}$ transition under a continuous cooling. That transition was also found to be reversible when the system was reheated in a similar continuous manner. This phase behaviour demonstrates that the observed $F_{ddd}$ microphases are thermodynamically robust equilibrium phases. We note that there have been no phase transformations observed when either of the two systems was heated or cooled across the boundaries separating the domains of the ordered periodic microphases. This can be explained by the close degeneracy of the free energies of different microphase morphologies at the same thermodynamic parameters [1, 6]. This degeneracy can also account for the significant metastability area between the lamellar and $F_{ddd}$ domains in the phase diagram of System I where both phases have been observed self-assembling.

mesophases [13, 14]. In $V_1$ the long-range repulsion is extended to a significantly larger distance than in $V_2$. In the following the systems using potentials $V_1$ and $V_2$ will be referred to as System I and System II, respectively.

We explored the phase behaviour of both systems by performing isochoric coolings within a range of densities starting from the isotropic liquid state equilibrated at high temperature. The cooling to the targeted points of the phase diagram was performed by independent discontinuous quenching steps with comprehensive equilibration following each step. Under cooling, both systems were found to perform liquid-gas microphase separation
It has been argued that the diffusion of the constituent polymer chains along the separating surface in the triply periodic networks formed by block copolymers is blocked by the strong separation effects [3, 5]. By contrast, the particles in the simulated Fddd morphologies demonstrate liquid-like diffusion. Fig.3 shows the Arrhenius plot of the diffusion rate in System II within the relevant range of temperatures. No significant difference in either the diffusion rate or the activation energy is observed upon the transition between the uniform liquid and the Fddd demonstrating the fluid nature of the observed microphase, see also [15]. We can thus conclude that this transition is a microphase separation within the liquid-gas spinodal domain as conjectured by Lebowitz and Penrose [1].

The structure factor of a system of \( N \) particles is defined as:

\[
S(Q) = \frac{1}{N} \left| \sum_{j=1}^{N} e^{iQr_j} \right|^2
\]

(2)

where \( r_j \) are the particle positions. To remove thermal fluctuations, the instantaneous particle configurations considered here have been subjected to the steepest-descent minimisation. Fig.4 shows the maxima of \( S(Q) \) for both systems in three characteristic \( Q \)-planes labelled by Miller indices \( hkl \). These patterns are consistent with the small-angle X-ray scattering measurements on the Fddd networks found in block copolymers [3, 16]. We note that this is the first 3D observed diffraction pattern of a Fddd network.

The positions of the observed maxima of \( S(Q) \) are related to the orthorhombic unit cell parameters \( a, b, c \) as \( Q_{hkl} = 2\pi(h/a, k/b, l/c) \). For the system I we found \((a : b : c) = (1 : 2.0 : 4.0)\), \( a = 4.3 \). For the system II the respective results are \((a : b : c) = (1 : 1.99 : 3.32)\), \( a = 3.49 \). The parameters’ ratios for the System II reproduce those found in the Fddd structures formed by block copolymers [5, 16] within the margin of the accuracy of measurements. For the System I, the ratio \( c/a \) appreciably exceeds the experimentally observed value [5], which can possibly be ascribed to the impact of the boundary conditions.

The Fddd unit-cell parameters are intimately related to the problem of thermodynamic stability of this orthorhombic microphase relative to the cubically symmetric gyroids. This symmetry breaking can be understood in terms of weak segregation theory [17]. The Landau expansion of the free energy in terms of composition modes demonstrates spinodal instability for the modes corresponding to the lattice parameters obeying the relation: \((a : b : c) = (1 : 2 : 2\sqrt(3))\) [18]. The lattice parameters for the system II agree with this relation quite closely, whereas for the system I the ratio \( c/a = 2 \) deviates from the one predicted by the theory. This can possibly account for the difference in their phase behaviour: System II demonstrated direct thermoreversible transformation for both systems in three characteristic \( Q \)-planes labelled by Miller indices \( hkl \). These patterns are consistent with the small-angle X-ray scattering measurements on the Fddd networks found in block copolymers [3, 16]. We note that this is the first 3D observed diffraction pattern of a Fddd network.

![FIG. 4: Isointensity contour plots of the structure factor for the two systems.](image)

![FIG. 5: A and B: the density isosurfaces for the systems I and II, respectively. C and D, respectively: the unit cells for the Systems I and II cut from the density isosurfaces. E: ball-and-stick model for System I, The (10,3) ring is highlighted.](image)
between the isotropic liquid phase and the \textit{Fddd} phase whereas for System I these two phases are separated by a domain of lamellar phase. Also, that system’s phase diagram demonstrated considerable overlap between the LAM and the \textit{Fddd} domains. The deviation of the \(c/a\) ratio in System I from the value minimising the free energy can possibly be explained by the constraints imposed by the periodic boundaries. On the other hand, the fact that despite this distortion the system still self-assemble into the \textit{Fddd} network can be viewed as the evidence of the robust nature of this transition.

It is convenient to present bicontinuous periodic morphologies in terms of the triply periodic surfaces segregating the two percolating domains. For the present morphology formed as a result of the liquid-gas microphase separation this would be the density isosurface. For that purpose, a continuous perfectly periodic real-space density distribution has been produced by the inverse Fourier transformation of the calculated structure factor, with the latter’s width constrained by a Gaussian window function of an appropriately chosen width. In this way sufficiently smooth uniform density isosurfaces have been produced eliminating the effects of the local fluctuations of the density distribution. These isosurfaces are shown in Fig.5 which also shows the unit cells of the simulated \textit{Fddd} periodic networks as cut fragments of the density isosurfaces.

The topology of triply periodic networks is commonly analysed in terms of skeletal graphs, ball-and-stick models \cite{16}. Such a model for the unit cell of System I is shown in Fig.5E. The stick lengths and positions have been produced as the best fits to the isosurface. According to the classification of Wells \cite{19}, triply periodic nets can be viewed as the tilings of space by closed loops of \(n\) nodes with \(p\) connections each, denoted as \((n,p)\).

The \textit{Fddd} nets were concluded to be composed of \((10,3)\) loops \cite{3}. Such a loop is highlighted in the ball-and-stick model shown in Fig.5E. Like in the experimentally observed \textit{Fddd} networks \cite{16}, the three-fold symmetry of the nodes is found to be broken with longer sticks oriented along the \(c\) axis.

We note that the distance between the longer sticks coincides with the parameter \(a\) of the unit cell. For both systems this distance is consistent with the long repulsion range of the respective potential. Thus we can rationalise the observed self-assembly of the \textit{Fddd} network in a simple system of particles as follows: the attraction part of the pair potential favours condensation whereas the range of its long repulsion part defines the basic periodicity of the network, its symmetry arises from the Landau free energy minimum as a result of the superposition of composition modes \cite{17, 18}.

We conclude with the following remarks.

1. It has been postulated that the entropic effects of polymer chain stretching are primarily responsible for the network morphologies in block copolymers. In particular they were suggested to account for the 3-fold connectors universally observed in these networks. The finding of this topology in simple systems suggests that a more general mechanism is responsible for its formation.

2. This is the first particle simulation of the \textit{Fddd} network. The detailed particle-level information about the geometry of its triply periodic domains can be expected to advance the development of the \textit{Fddd} minimal surface which hasn’t been reported so far.

3. The self-assembly of the \textit{Fddd} network in two distinctly different simple systems within a range of densities evidences the robust nature of this phase transition. This form of the pair potential can be expected to produce other triply periodic networks in simple systems including colloids where the interparticle interactions can be tuned to approximate it.

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