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Self-assembly of a triply periodic continuous mesophase with $Fddd$ symmetry in simple one-component liquids

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Triply periodic continuous morphologies (networks) 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 where two simple one-component liquids form upon cooling an equilibrium network with the $Fddd$ space group symmetry. This complexity reduction in the liquid network formation in terms of the particle geometry and the number of components evidences the generic nature of this class of phase transition suggesting opportunities for producing these structures in a variety of new systems.

The concept of microphase separation in fluids was introduced more than fifty years ago by Lebowitz and Penrose[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 that fluids of immiscible macromolecules may be partitioned into mesoscopic-scale infinitely continuous domains by minimal hyperbolic surfaces[2] which are free of self-intersection and translationally ordered (triply periodic). This phase separation have been observed in block co-polymer melts producing a variety of multiply continuous triply periodic morphologies which are both elegant and remarkably useful for photonic applications[3–5]. As a surprising discovery, the orthorhombic $Fddd$ network was observed[6,7], 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 minimization of the inter-domain surface area and the conformation entropy of the molecular chains. An entropic stabilisation was concluded in a gyroid phase produced in a model of non-spherical particles[8]. 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[9,10] predicted that triply periodic networks can be stabilized 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[11]. However, despite the extensive experimental efforts, triply periodic morphologies have never been observed in colloidal systems.[12,13].

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[14–20]. Moreover, it was concluded, based on the density-functional calculations[10], that if one starts with a random particle configuration, such a system, due to the complexity of its free-energy landscape, would not 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. For both systems, the phase diagrams include density-temperature domains where they self-assemble into an equilibrium triply periodic morphology possessing orthorhombic $Fddd$ space-group symmetry.

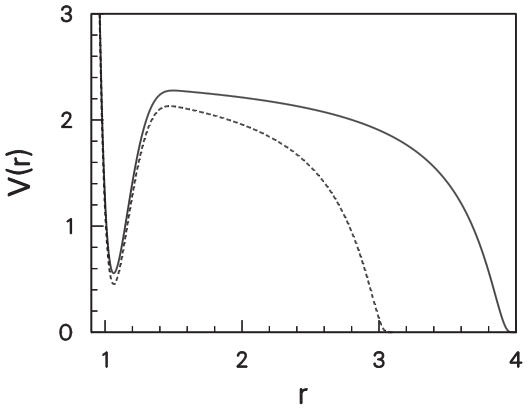

FIG. 1. Pair potentials used in this study. Solid line, V_1; dashed line, V_2.

Each of the investigated molecular-dynamics models was composed of 16384 identical particles confined to a cubic box with periodic boundary conditions. The potential energy for two particles separated by the distance r is described by the

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functional form:

$$V(r) = a_1(r^{-m} - d)H(r,b_1,c_1) + a_2 H(r,b_2,c_2) \quad (1)$$

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

	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.

We used two pair potentials, V_1 and V_2 shown in Fig. 1 with parameters presented in Table I. The simulation reduced units were those used in the definition of the potentials, and the time step was 0.002.

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 mesophases[21,22]. 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 behavior 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. Each step was followed by an equilibration run of 2 millions time steps which corresponded to the mean-square displacement of about 1500 (the unit of length is approximately the particle diameter). Under cooling, both systems were found to perform liquid-gas microphase separation 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 classical morphologies, lamellae and hexagonally packed cylinders, both systems exhibit domains where the transitions produce equilibrium triply periodic networks with the $Fddd$ space group symmetry. An instantaneous particle configuration of this microphase produced by System I is shown in Fig. 3b. In the following we present a detailed analysis of the structure and the dynamical properties of the these $Fddd$ morphologies.

A difference in the phase behavior of the two systems can be observed. For System I, the $Fddd$ domain is separated from the uniform liquid domain by a domain of lamellar phase. Thus, it was only possible to produce the $Fddd$ self-assembly by its discontinuous quenching from the equilibrium liquid state to a targeted range of temperatures.

System II performed the liquid-$Fddd$ transition under a continuous cooling, and it was also found to be reversible when the system was reheated in a similar continuous manner. This phase behavior demonstrates that the observed $Fddd$ microphases are thermodynamically robust equilibrium phases.

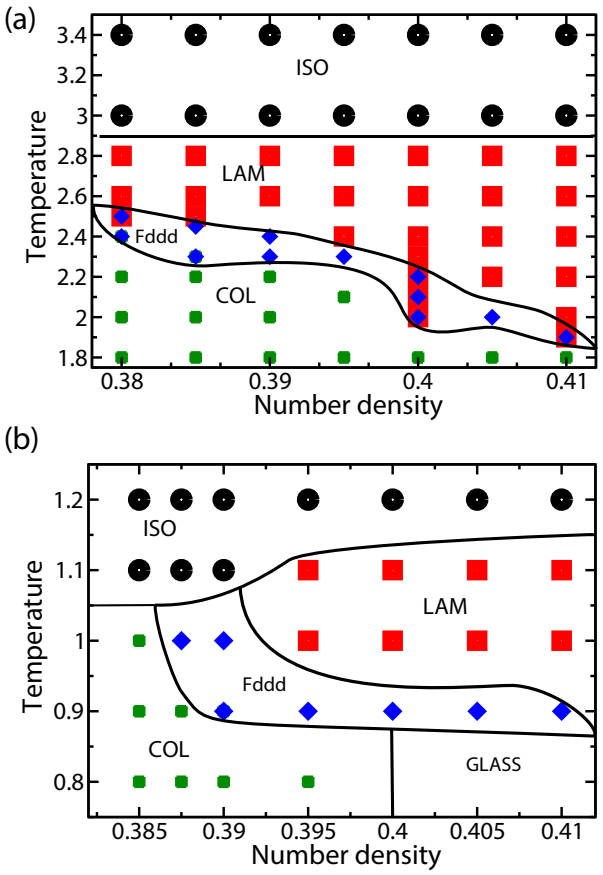

FIG. 2. Phase diagrams of the simulated systems. (a) and (b), respectively, System I and System II. Open circles: isotropic liquid (ISO). Open squares: lamellar phase (LAM). Diamomds: $Fddd$. Crosses: columnar phase (COL). The solids lines are guides to the eye.

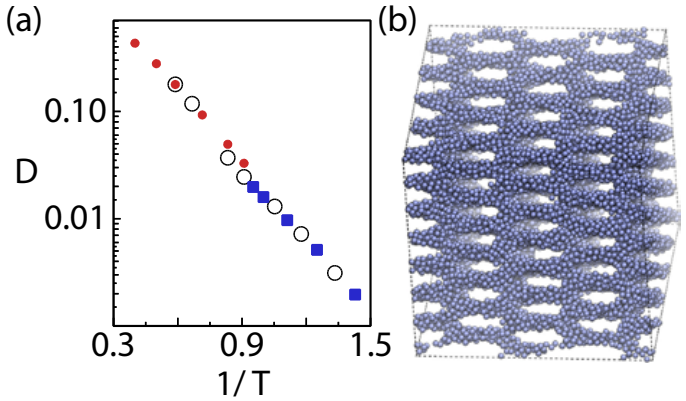

FIG. 3. (a) Arrhenius plot for System II at $\rho = 0.39$. Dots: isotropic liquid; squares: $Fddd$ phase, cooling; open circles: $Fddd$ phase, reheating. (b) An instantaneous particle configuration of the $Fddd$ phase formed in System I at $\rho = 0.395$ and $T = 2.3$.

No phase transformations have been observed when either of the two systems was heated or cooled across the the domain boundaries separating the periodic microphases, after a relax-

ation time of 3 millions time steps.

This can be explained by the close degeneracy of the free energies of different microphase morphologies at the same thermodynamic parameters[1,10]. It can also account for the significant metastability area between the lamellar and $Fddd$ domains in the phase diagram of System I where both phases have been observed self-assembling.

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[3,7]. By contrast, the simulated $Fddd$ morphologies demonstrate liquid-like diffusion. Fig. 3 shows the Arrhenius plot of the diffusion in System II; some points represent metastable $Fddd$ states produced by heating and cooling across its domain boundaries which, as mentioned above, doesn't result in a phase transition. 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 Ref.[23] and Supplementary Material). We can thus conclude that this transition is a microphase separation within the liquid-gas spinodal domain as conjectured in[1].

We investigated two $Fddd$ configurations: one produced by System I at the density $\rho = 0.395$ and temperature $T = 2.3$, the other by System II at $\rho = 0.39$ and $T = 1.0$. To remove thermal fluctuations, the configurations have been subjected to the steepest-descent minimization. For N particles positioned at $\mathbf{r_j}$ the structure factor is defined as:

$$S(\mathbf{Q}) = \frac{1}{N}\left|\sum_{j=1}^{N} e^{i\mathbf{Q}\mathbf{r}_j}\right|^2 \qquad (2)$$

Fig. 4 shows the maxima of $S(\mathbf{Q})$ for both systems in three characteristic Q-planes labelled by Miller indices hkl. These patterns are consistent with the the small-angle X-ray scattering measurements on the $Fddd$ networks in block copolymers[3,24]. This is the first observation of the 3D diffraction pattern of a $Fddd$ network.

The positions of the observed maxima of $S(\mathbf{Q})$ are related to the orthorhombic unit cell parameters a,b,c as $\mathbf{Q}_{hkl} = 2\pi(h/a, k/b, l/c)$. 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[7,24] within the margin of the accuracy of measurements. For the System I, the ratio c/a appreciably exceeds the experimentally observed value[7], 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[25]. 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: $(a:b:c) = (1:2:2\sqrt{(3)})$[26]. The lattice parameters for the system II agree with this relation quite closely,

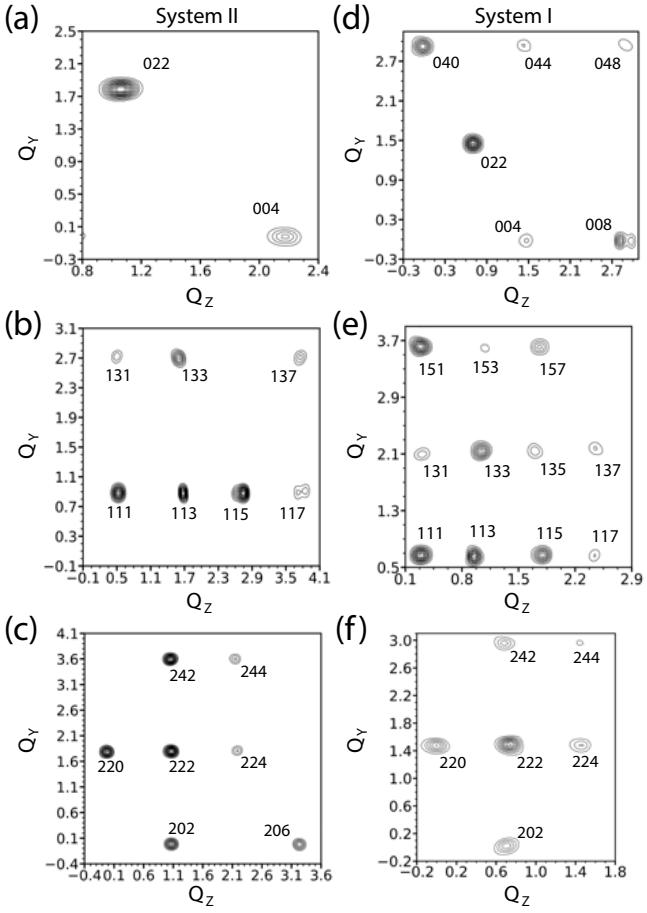

FIG. 4. Isointensity contour plots of the $S(Q)$ maxima labelled by Miller indices, (a)-(c) and (d)-(f) represent systems II and I, respectively.

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 behavior: System II demonstrated direct thermoreversible transformation between the isotropic liquid phase and the $Fddd$ 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 $Fddd$ 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 $Fddd$ 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 Gaus-

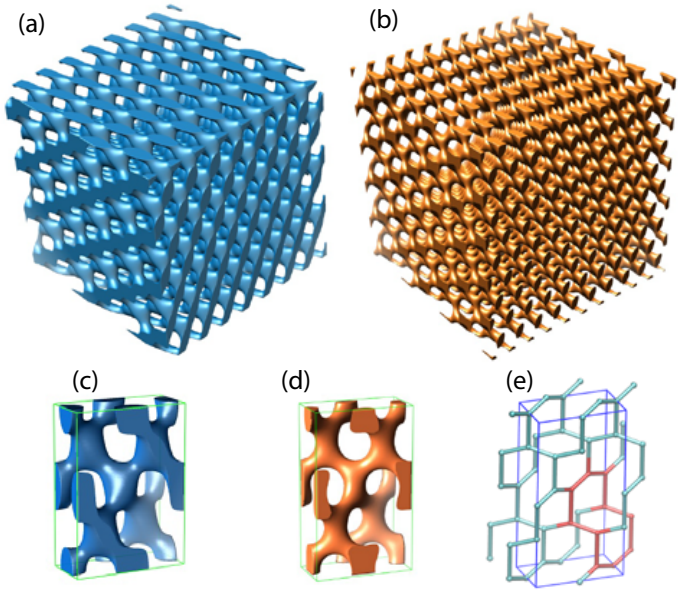

FIG. 5. (a) and (b): the density isosurfaces for the systems I and II, respectively. (c) and (d), respectively: the unit cells for the Systems I and II cut from the density isosurfaces. (e): ball- and-stick model for System I, The (10,3) ring is highlighted.

sian window function of an appropriately chosen width. In this way sufficiently smooth uniform density isosurfaces have beeen 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 $Fddd$ 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[24]. Such a model for the unit cell of System I is shown in Fig. 5(e). The stick lengths and positions have been produced as the best fits to the isosurface. According to the classification of Wells[27], 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 $Fddd$ nets were concluded to be composed of $(10,3)$ loops[3]. Such a loop is highlighted in the ball-and-stick model shown in Fig. 5(e). Like in the experimentally observed $Fddd$ networks[24], 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 $Fddd$ 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[25,26]

We conclude with the following remarks.

1. The network topologies in block copolymers were argued to be governed by the balance between the interface area minimization and the entropy of polymer chain stretching[3]. In particular, the latter was suggested to account for the 3-fold connectors universally observed in these networks. The finding of this topology formed in the systems of identical spherical particles dramatically reduces the complexity of the transition suggesting a more general mechanism of the network formation, with significant conceptual and practical implications.
2. This is the first particle simulation of the $Fddd$ network. The detailed particle-level information about the geometry of its triply periodic domains can be expected to advance the development of the $Fddd$ minimal surface which hasn't been reported so far.
3. The self-assembly of the $Fddd$ network in two distinctly different simple systems within a range of densities evidences the robust nature of this phase transition. This model potential provides a different route to the microphase separation networks than that in block copolymers. This route can be expected in colloids where the interparticle interactions can be tuned to approximate this potential. Colloidal particles with competing interaction were found to form clusters and gel[12,28], but all the attempts to produce extended periodic microphases predicted by theoretical models have been unsuccessful. The problems of exact control of the interparticle interactions and the sluggishness of the relaxation dynamics were suggested as possible explanations of this failure. By directly linking the interaction potential to the phase behaviour this simulation can properly guide the experimental efforts aimed at producing triply periodic mesophases in colloids.

Supplementary Material

It contains: the Radial Distribution Functions and the Structure Factors for System I and II (Fig. S1,S2); the Mean Square Displacement for the two systems (Fig. S3); the $Fddd$ transition for system II in the energy-temperature phase diagram (Fig. S4); two particle configurations for system II when the $Fddd$ phase is produced in a NVT and NPT ensemble (Fig. S5, S6); a configuration of the NPT simulation containing 131072 particles for System II and the $Fddd$ cluster formation (Fig. S7); the link to the movie showing the dynamical trajectory of the $Fddd$ phase for system I (Fig. S8).

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Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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