Electronic Supplementary Information

Defect Transition of Smectic Liquid Crystals Confined in Spherical Cavities

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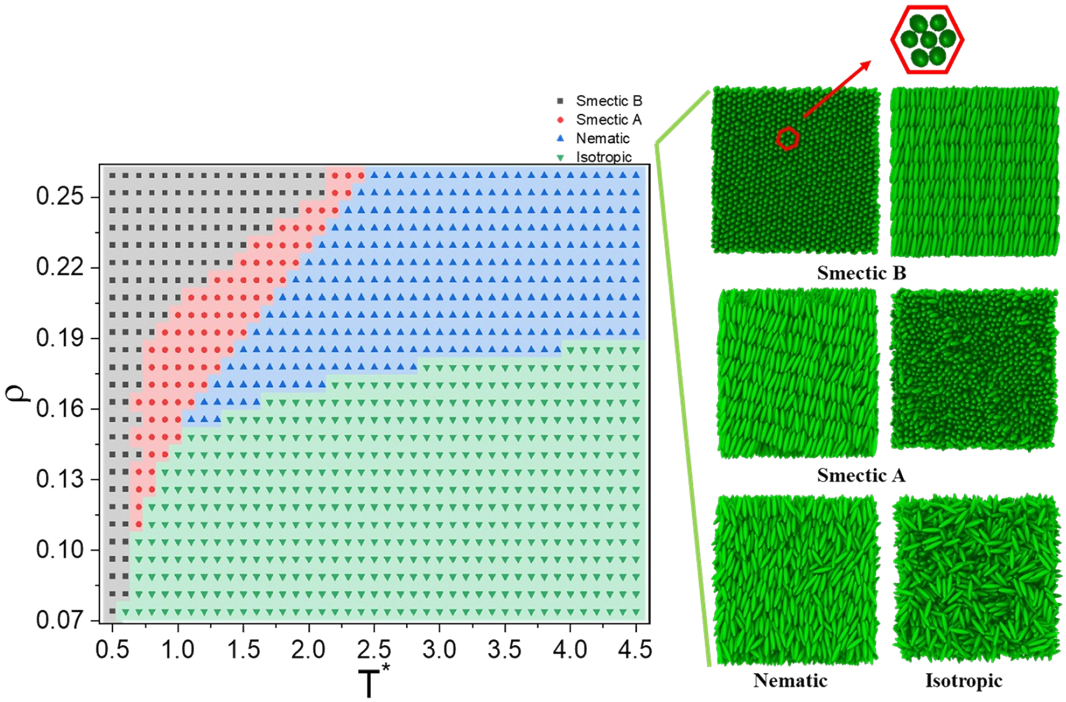

Figure S1: Phase diagram in the plane with temperature and number density (T^*-ρ) in the bulk at NVT ensemble. There are four phases, including isotropic (I), nematic (N), smectic-A (SmA), and smectic-B (SmB). The picture on the right shows the phase structure. In this work, we only studied the structures of LCs at $T^* = 1.0$, including the bulk and LCs confined in the spherical cavity, and we found three phase structures, except for N phase, which means that LCs undergo a discontinuous phase transition of I-SmA as the density of LCs increases. E. de Miguel[1,2] also proved that I phase can be directly transformed into the SmA phase with a discontinuous phase transition at low temperature in the NVT ensemble.

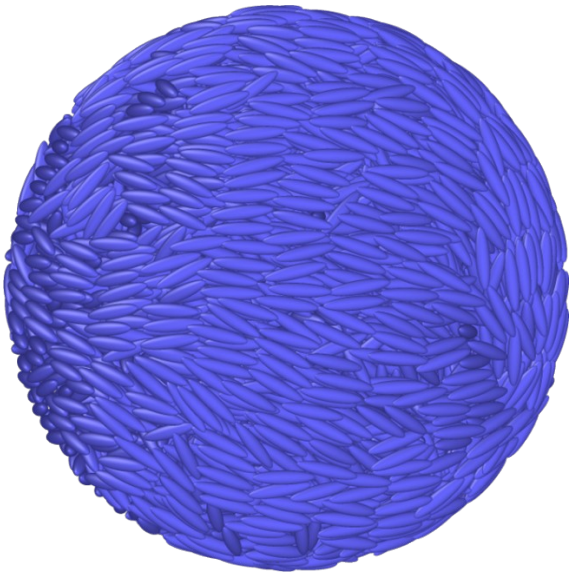

Figure S2: The snapshot of spherical confined liquid crystals with ρ=0.15, that shows a coexisting of nematic/smectic regions,

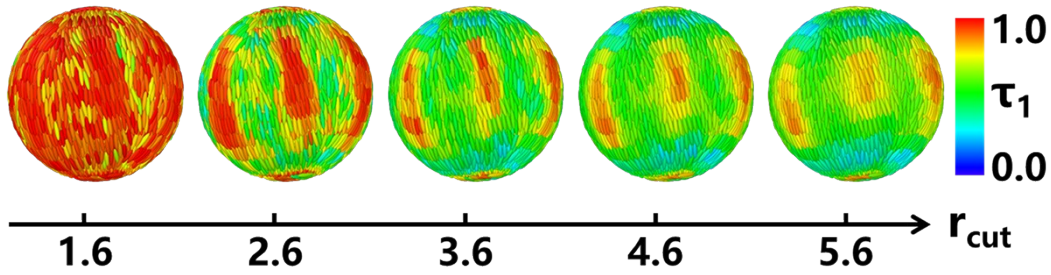

Figure S3: Through calculating the local translational order parameter τ_1, the structure of Smectic-B phase LC (ρ = 0.25) confined in the spherical cavity is characterized, in which the range r_{cut} is changed from $1.6\sigma_0$ to $5.6\sigma_0$. The color of the particle was adjusted by the value of τ_1 (the range of τ_1: 0.0~1.0).

We find that the striped textures have an arrangement of nematic and smectic phases, and $\langle\tau\rangle$ can be used to distinguish between nematic and smectic phases (Compared with nematic LCs, smectic LCs not only have directional order, but also have layered structure.). Therefore, the local translational order parameter τ_1 of each particle i, defined as $\langle\tau\rangle$ over particles falling in a sphere with center r_i and radius r_{cut}, is introduced to characterize the inhomogeneities.

Figure S2 illustrates our choice of numerical values for r_{cut}. Through the comparison of all structures, we find that the defect characterized by τ_1 at $r_{cut} = 2.6\sigma_0$ is more obvious. Thus, we use this value to analyze the later findings accordingly, which can qualitatively characterize this real existing inhomogeneities.

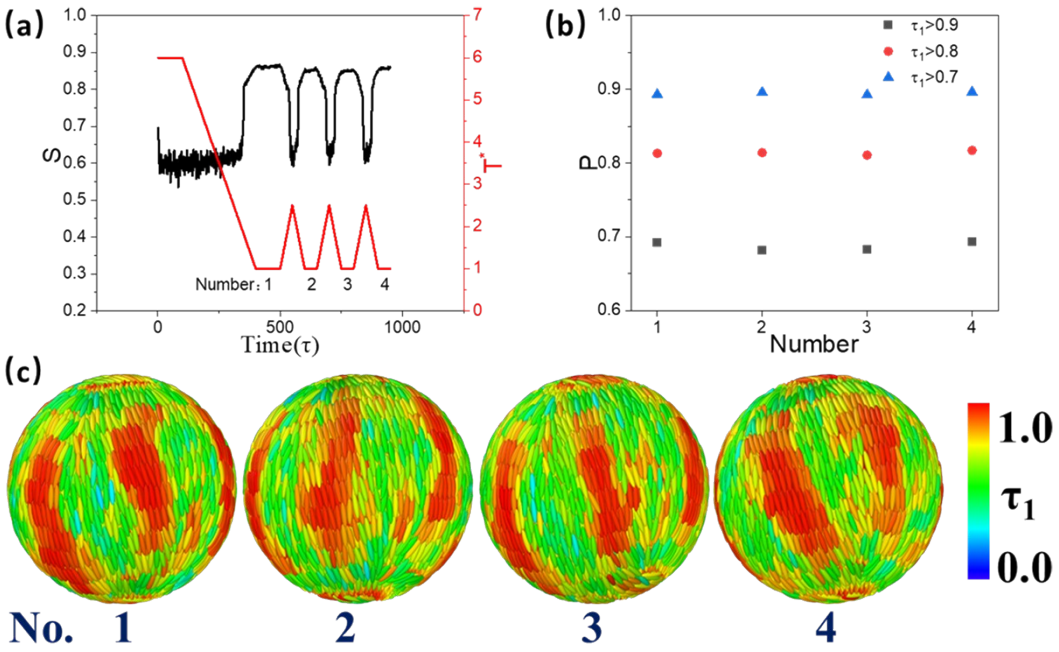

Figure S4: The inhomogeneities of confined SmB phase LCs (ρ = 0.25) through iterative annealing. The structures after stabilization are numbered 1, 2, 3, and 4. (a) The red solid line indicates the way of annealing (T^* varies with Time.). The black solid line represents the change of S with Time. S has a plateau value, indicating that the structure has stabilized. (b) The proportion P of particles whose τ_1 is greater than 0.9, 0.8, and 0.7 about four structures (No. 1, 2, 3, 4.). And the value of P with different numbers is the same, indicating that the inhomogeneities are stable and will not disappear under certain conditions. (c) The inhomogeneities with different numbers are characterized by τ_1.

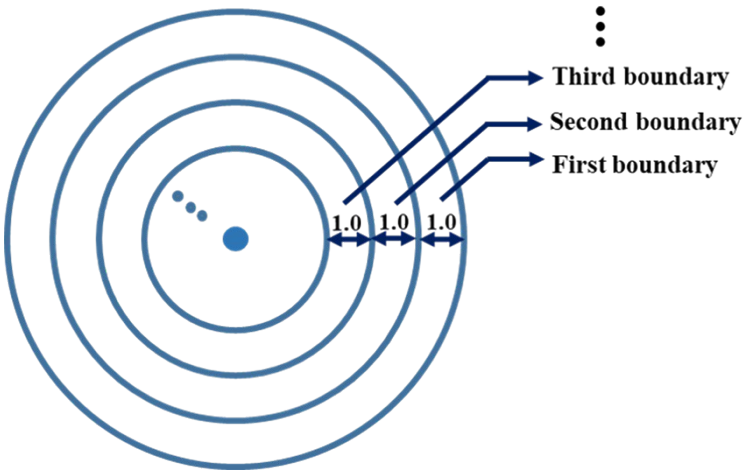

Figure S5: The method of dividing the layers from the shell to the center of the confined system. The interval between layers is equal to $1.0\sigma_0$ because of GB particles with $a_i = b_i = 1.0\sigma_0$. The divided regions are shell structures.

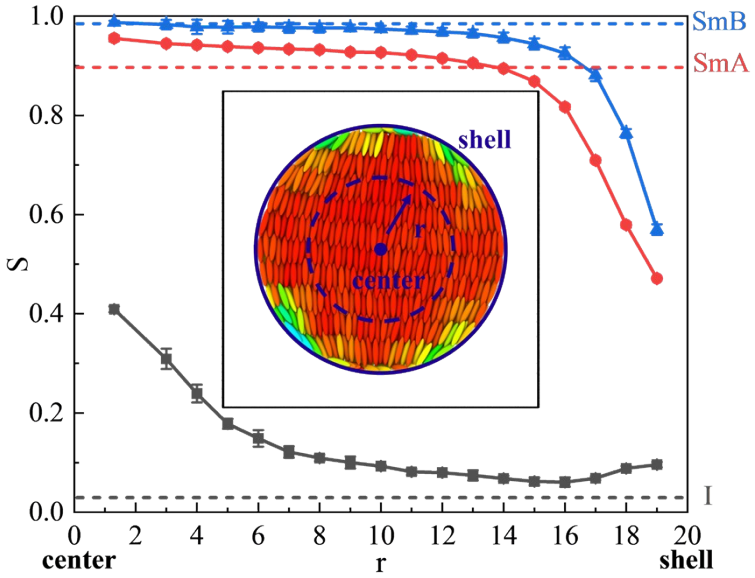

Figure S6: The orientational order parameter S as a function of *r* under spherical confinement condition, including isotropic phase with ρ=0.12, smectic-A phase with ρ=0.18, and smectic-B phase with ρ=0.25. Short dashed lines represent S of the bulk. The illustration shows the calculation range of S that is within a shell [r − 0.5; r +0.5] from the center (blue dashed circle, the method in Figure S4.).

We analyze the change of S value from the center of sphere to the spherical shell in the figure. From center to shell, the initial changes in S of SmA and SmB are small and insignificant, and SmA's S is slightly larger than that of the bulk. However, curved surface of the spherical shell does not favor the direction **n**. It also shows that the influencing region of the spherical shell on smectic phase LCs is mainly near the spherical shell, and the internal LCs are affected to a small extent. The higher part (black solid line with r < 6) of confined I phase than that of the bulk, is mainly caused by the small number of particles in the calculation area (only a few particles) which is not applicable to this calculation method. Moreover, S of the confined system is larger than that of the bulk near r = 20, since the LC molecules tend to orientate along the spherical shell in I phase.

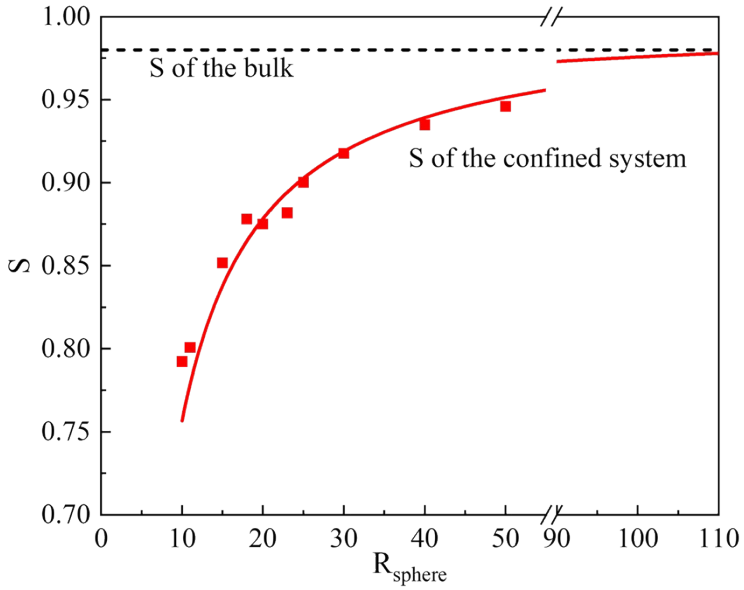

Figure S7：The orientational order parameter S value of the confined system depending on the radius of the spherical shell (R_{sphere}). Red solid line is fitted with $S = k * \frac{-3}{R} + S_0 (S_0 = 1.0,\ k = 0.81 \pm 0.01)$.

Under spherical confinement, the orientation of LC molecules is closely related to the curvature of the spherical shell at the boundary. As the radius increases, the surface area to volume ratio (3/R) of the spherical shell gradually decreases, and the influence of spherical shell on the orientation of LCs is gradually reduced (because S of LCs is increasing.). Thus, we tried to fit the relationship between S and R_{sphere} by the negative correlation function of the ratio (3/R). It can be seen from the fitting curve that the influence of spherical shell on the overall LCs is slowly diminishing with the radius increasing, and S value is close to that of the bulk at $R_{sphere} = 100\sigma_0$ on the extension line of the fitting curve.

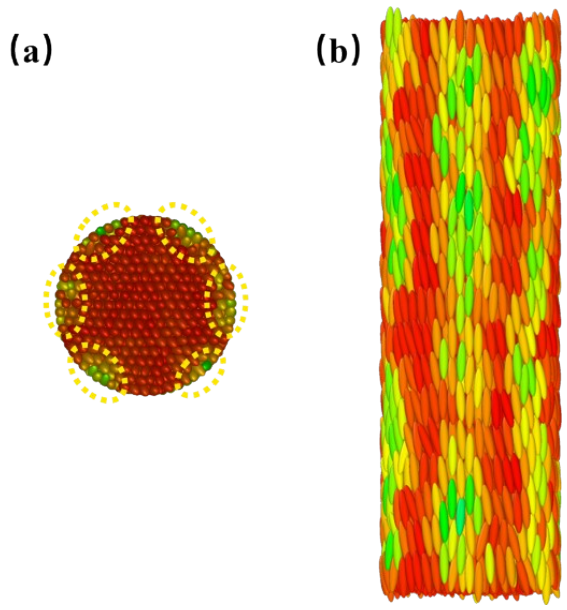

Figure S8: Schematic illustration of Smectic-B phase LCs with ρ*=0.25 and the radius as 10 under cylindrical confinement, (a) top view, (b) front view.

Table S1: The simulation details of SmB phase LC (ρ = 0.25) confined in the spherical cavity with different radius.

sample	Ideal radius (σ_0)	Real radius (σ_0)	Number of LJ particles	Volume of spherical cavity (σ_0^3)	Number of GB particles
1	10	9.98	1242	3838	954
2	15	14.96	2792	13293	3302
3	20	20.00	4992	32203	8000
4	25	24.81	7682	61958	15392
5	30	29.46	10832	104264	25901
6	40	40.31	20282	269054	66840
7	50	51.16	32672	552340	137220

The number density of the spherical shell is 0.99 (Number of LJ particles is divided by the surface area of the spherical shell.). The volume of the spherical cavity is calculated as the volume of the sphere ($^4/_3\pi R^3$) subtracting the volume of half of all LJ particles inside the sphere. Real radius is used in all calculations. The spherical shell is formed by the arrangement of LJ particles with icosahedral symmetry, which is taken from the reference (R. H. Hardin, N. J. A. Sloane and W. D. Smith, Tables of spherical codes with icosahedral symmetry, published electronically at http://NeilSloane.com/icosahedral.codes/.).

References

[1] E. de Miguel, E. Martín del Río and F. J. Blas, The Journal of Chemical Physics, 2004, 121, 11183–11194.

[2] J. T. Brown, M. P. Allen, E. Martín del Río and E. de Miguel, Phys. Rev. E, 1998, 57, 6685–6699.