Electronic Supplementary Material (ESI) for Soft Matter

The effects of pressure and temperature on the energetics and pivotal surface in a gyroid inverse bicontinuous cubic phase

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Supplementary information:

Calculation of lipid compressibility:

The lipid compressibility is obtained from equation S1.

$$B_{ad} = -\frac{1}{V_n}\left(\frac{dV_n}{dP}\right) \qquad [S1]$$

Where B_{ad} is the adiabatic compressibility of the volume occupied between the pivotal surface and the bilayer midplane; $(V_n)_{Pim}$ = 619.5 Å^3 and $(V_n)_{CMCM}$ = 595.5 Å^3 (obtained from fitting experimental data (Table 5) and $\left(\frac{dV_n}{dP}\right)_{PIM} = 1.03 \times 10^{-4}$ Å^3 kbar^{-1} and $\left(\frac{dV_n}{dP}\right)_{CMCM} = 1.2 \times 10^{-4}$ Å^3 kbar^{-1} obtained from weighted linear fits to the experimental data.

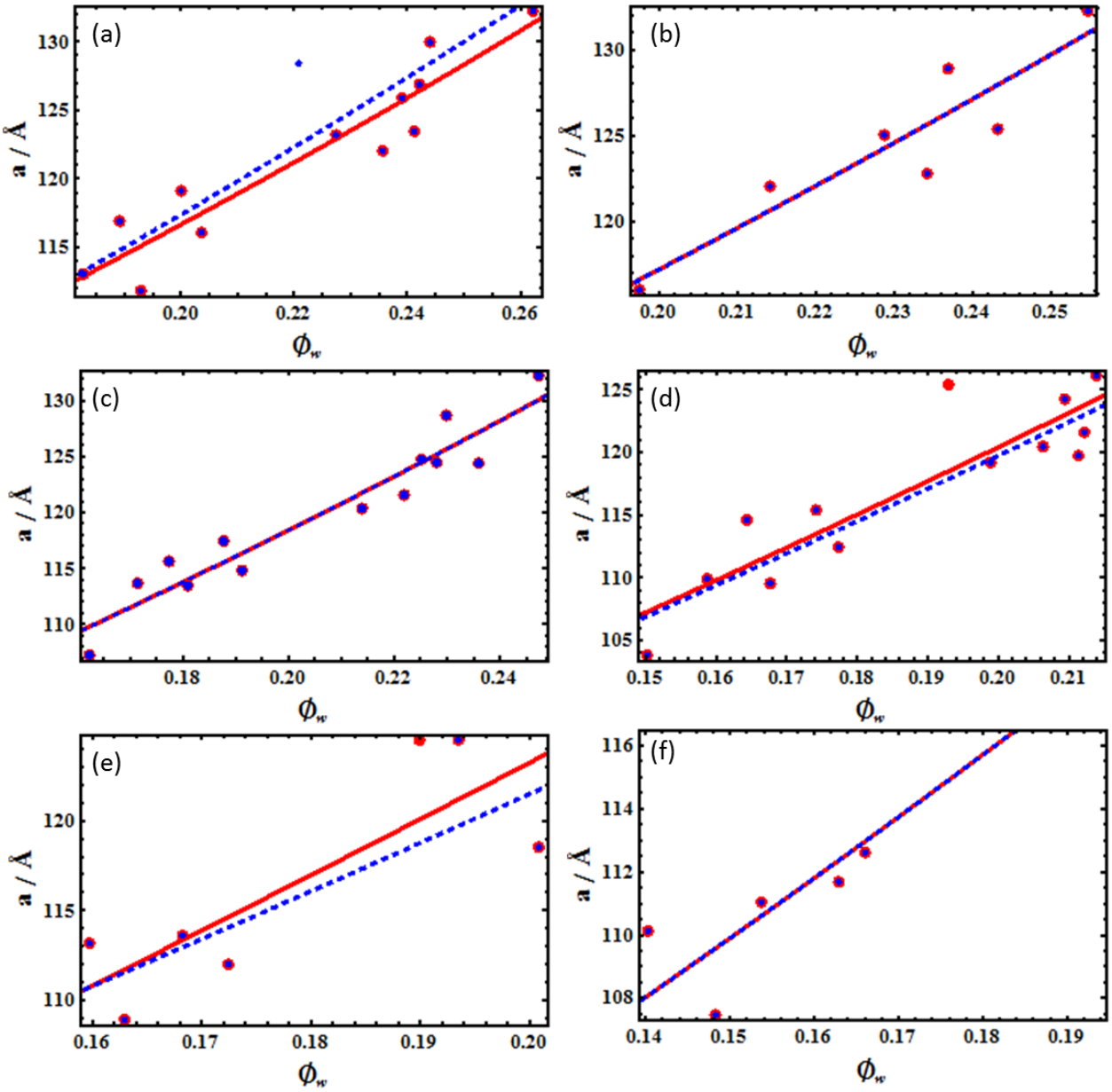

Figure S1: Experimental data (blue dots), and pivotal surface theory fits for the constant mean curvature model (CMCM) (blue dotted line) and the parallel interface model (PIM) (red line) to swelling data obtained for the Q_{II}^{G} phase in monolinolein at a) 10°C, b) 15°C, c) 20°C, d) 25°C, e) 30°C, f) 35°C

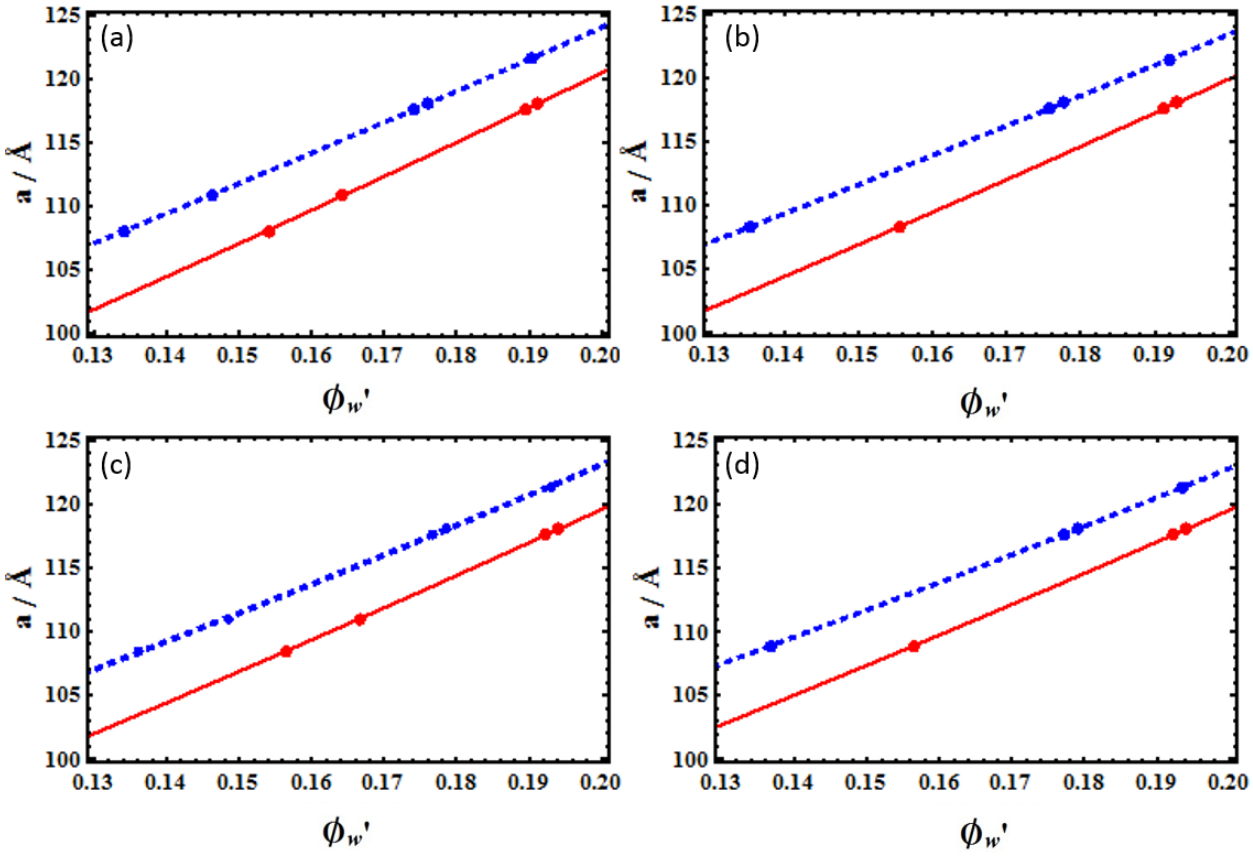

Figure S2: Pivotal surface theory fits for the parallel interface model (CMCM) (blue dotted line) and the constant mean curvature model (PIM) (red line) to swelling data obtained for the Q_{II}^{G} phase in monolinolein at 30°C and a) 1 bar, b) 200 bar, c) 400 bar and d) 600 bar.

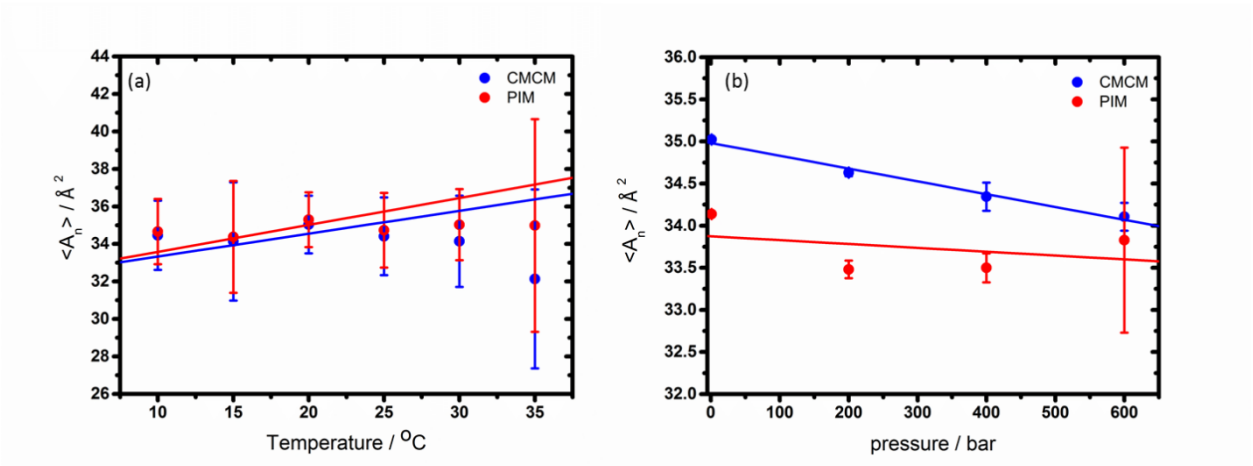

Figure S3: The effect on A_n of (a) temperature, (b) pressure, obtained by fitting of the CMCM (blue) and PIM (red). As the position of the pivotal surface changes, A_n adjusts to reflect movement up and down the lipid and a weighted linear fit shows that there is a pressure and temperature dependent shift in A_n. The model assumes that the density is uniform along the length of the lipid, and therefore if the phase swells the lipid will stretch as the interfacial curvature decreases in order to maintain a constant molecular density. In reality the density at the head group and the tail will not be the same. It is therefore difficult to find physical meaning for the changes to the area at the pivotal surface as

temperature is changed. Moreover any temperature dependence of A_n is within the error of the data points. The values obtained for A_n are comparable to those obtained previously in comparable systems and confirms the accuracy of the model fits to our experimental data [1,2].

T/°C \ p/ bar	1	100	200	300	400	500	600	700
10	639±8	648±4	642±3	640±2	638±4	637±3	642±3	641±6
15	656±9	659±5	653±3	650±3	647±5	646±3	649±4	648±6
20	673±10	670±5	664±3	659±3	657±5	655±4	656 ±4	656±7
25	690±11	682±6	675±4	669±3	666±6	664±4	665±5	663±8
30	707±12	694±6	686±4	678±4	675±6	673±5	671±5	671±9
35	724±13	705±7	697.±4	688±4	685±7	682±5	678±6	678±10
40	742±14	716±7	708±5	697±4	694±8	691±6	685±6	686±11
45	759±15	728±8	719±5	707±5	704±8	700±6	692±6	693±12

Table S1. Summary of molecular volume data (Å^3) at varying pressures and temperatures obtained from linear fits to the experimental density data.

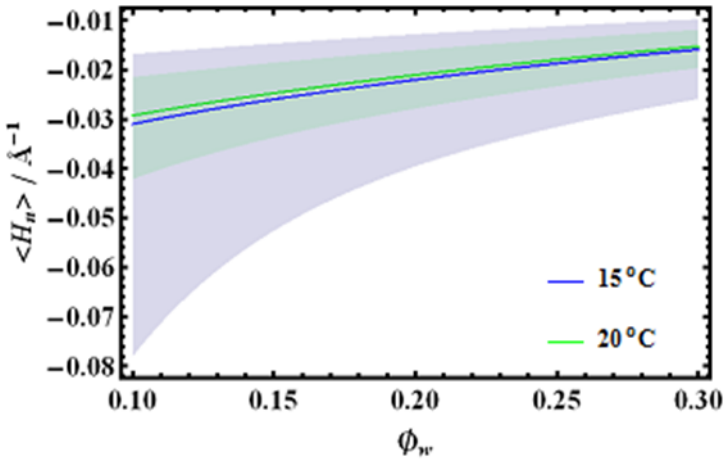

Figure S4 . Surface averaged mean curvature and the its error calculated for bilayers constrained to a constant mean curvature interface using the pivotal surface parameters . The shaded region shows the error in the $<H_n>$, green for 20 °C and blue for 15 °C.

APPENDIX A: THE GEOMETRICAL MODELS

The parallel interface model constrains the geometry of the pivotal surface so it is parallel to the bilayer midplane. It is derived through defining an area of a patch $A(\xi)$ on a parallel surface, ξ from the minimal surface, and relating this to an original patch A(0) on the minimal surface:

$$\boldsymbol{A(\xi) = A(0)(1 + K\,\xi^2)} \qquad \text{[S2]}$$

where K is the Gaussian Curvature.

Then defining the volume occupied by the patch and its projection from the minimal surface:

$$\boldsymbol{v(\xi) = A(0)\xi\,(1 + \frac{1}{3}K\,\xi^2)} \qquad \text{[S3]}$$

The patch on the parallel surface $A(\xi)$ can be translated to an area on the pivotal surface A_n, and $v(\xi)$ can be translated to V_n, the volume between the minimal surface, and the pivotal surface where ξ is the distance between the pivotal surface and the minimal surface.

In this model the curvature is inhomogeneous over the surface and it is appropriate to define the Gaussian curvature, K, A_n and V_n as surface averaged $\langle K\rangle$, $\langle A_n\rangle$, $\langle V_n\rangle$ respectively.

Combining Equation S2 and Equation S3 gives

$$\frac{\langle A_n\rangle}{\langle v_n\rangle} = \frac{1}{\xi}\left(\frac{1+\langle K\rangle\xi^2}{1+\frac{1}{3}\langle K\rangle\xi^2}\right) \qquad \text{[S4]}$$

<K> can be related to the geometry of the surface using the Gauss-Bonnet theorem (Equation S5)

$$\boldsymbol{\langle K\rangle = \frac{2\pi\chi}{\sigma_0 a^2}} \qquad \textbf{[S5]}$$

The variation of ξ with water volume fraction, ϕ_w, is then determined by the following equation S6 [1].

$$\boldsymbol{\frac{\langle v_n\rangle}{\langle V\rangle}\,(1-\phi_w) = \;2\,\sigma_0\left(\frac{\xi}{a}\right) + \frac{4}{3}\,\pi\,\chi\left(\frac{\xi}{a}\right)^3} \qquad \textbf{[S6]}$$

Combining Equations S4- S6 and solving gives a relationship between the lattice parameter (a), water volume fraction ($\emptyset_w$) of the phase and the pivotal surface parameters (A_n, V_n, V) (Equation S7).

$$a = \frac{< v_n >}{< A_n > (1-\phi_w)} \left(-2\sigma + \frac{2^{\frac{5}{3}}\sigma^2}{\left(4\sigma^3 + 9\pi\chi(1-\phi_w)^2\left(\frac{< v_n >}{< V >}\right)^2 + 3(1-\phi_w)\left(\frac{< v_n >}{< V >}\right)\sqrt{\pi\chi\left(8\sigma^3 + 9\pi\chi(1-\phi_w)^2\left(\frac{< v_n >}{< V >}\right)^2\right)}\right)^{\frac{1}{3}}} + 2^{\frac{1}{3}} \Big/ \left(4\sigma^3 + 9\pi\chi(1-\phi_w)^2\left(\frac{< v_n >}{< V >}\right)^2 + 3(1-\phi_w)\left(\frac{< v_n >}{< V >}\right)\sqrt{\pi\chi\left(8\sigma^3 + 9\pi\chi(1-\phi_w)^2\left(\frac{< v_n >}{< V >}\right)^2\right)}\right)^{\frac{1}{3}} \right)$$

[S7]

ϕ_w is the water volume fraction and can be calculated from the water content (wt % water) from Equation S8

$$\boldsymbol{\phi_w = \frac{C_w}{C_w + ((1-C_w) * (\frac{\rho_w}{\rho_l}))}} \qquad \textbf{[S8]}\ [1]$$

Where C_w is the water content (wt% water); ρ_w is the density of water; ρ_l is the density of lipid.

Using this geometric model the pivotal surface parameters for an inverse bicontinuous cubic phase, A_n, V_n and V, can be obtained by fitting to the swelling behavior of the Q_{II}^G phase.

Constant mean curvature model (CMCM)

The constant mean curvature model describes an interface where the bilayer and the pivotal surface are constrained to a constant curvature over the surface, the hydrocarbon chains are forced to stretch and compress to account for this and the variance in chain length requires energy. Like the pivotal surface model, relationships need to be made between the pivotal surface parameters and experimental data. Surface Evolver[2], a programme which 'evolves' a surface to its minimum energy, was used to calculate the curvature, volumes and surface areas of the minimised constant mean curvature structures at varying water contents. The computed dimensionless surface area and

curvature are obtained for surfaces with increasing water contents and the results are fitted to a power series of ϕ_n ($\phi_n = \frac{v_n}{V}(1-\phi_w)$), to obtain Equation S9 [3-5]

$$S_n = a^2 \sum_{i=0} \sigma_i \phi_n^{2i} \qquad [S9]$$

Where S_n is the area of the pivotal surface, a is the lattice parameter, and the σ_i are given by: σ_0 = 3.0915; σ_1 = -1.3317; σ_2 = -0.19974; σ_3 = -0.80113.

The area of the pivotal surface of a monolayer in a unit cell is given by Equation S10

$$S_n = \frac{A_n}{2}\frac{a^3(1-\phi_w)}{V} \qquad [S10]$$

Combining Equations S9 and Equation S10 the following relationship between the pivotal surface parameters (A_n, V_n, V), water volume fraction (φ_w) and lattice parameter is obtained.

$$a = 2 \sum_{i=0} \frac{\sigma_i[(\frac{v_n}{V})(1-\phi_w)]^{2i}}{(\frac{A_n}{V})(1-\phi_w)} \qquad [S11]$$

Using Equation S11, the properties of the constant mean curvature model can be obtained from experimental swelling data which have been obtained for the monolinolein system.

References:

1. R. H. Templer, *Langmuir*, 1995, **11**, 334-340.
2. D. C. Turner, Z.-G. Wang, S. M. Gruner, D. A. Mannock and R. N. McElhaney, *J. Phys. II France*, 1992, **2**, 2039-2063.
3. K. A. Brakke, *Exp. Math.*, 1992, **1**, 141.
4. D. M. Anderson, S. M. Gruner and S. Leibler, *Proceedings of the National Academy of Sciences of the United States of America*, 1988, **85**, 5364-5368.
5. K. Grosse-Brauckmann, *Journal of Colloid and Interface Science*, 1997, **187**, 418-428.
6. G. C. Shearman, B. J. Khoo, M.-L. Motherwell, K. A. Brakke, O. Ces, C. E. Conn, J. M. Seddon and R. H. Templer, *Langmuir*, 2007, **23**, 7276-7285.