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.

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

Where \( B_{ad} \) is the adiabatic compressibility of the volume occupied between the pivotal surface and the bilayer midplane; \( (V_n)_{Pim} = 619.5 \text{ Å}^3 \) and \( (V_n)_{CMCM} = 595.5 \text{ Å}^3 \) (obtained from fitting experimental data (Table 5) and \( \left( \frac{dV_n}{dP} \right)_{PIM} = 1.03 \times 10^{-4} \text{ Å}^3 \text{ kbar}^{-1} \) and \( \left( \frac{dV_n}{dP} \right)_{CMCM} = 1.2 \times 10^{-4} \text{ Å}^3 \text{ kbar}^{-1} \) 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 QII 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 $^{1,2}$.

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Table S1. Summary of molecular volume data ($\text{Å}^3$) 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 $\langle H_n \rangle$, 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, $\xi$ from the minimal surface, and relating this to an original patch $A(0)$ on the minimal surface:
\[ A(\xi) = A(0)(1 + K\xi^2) \]  

[S2]

where \( K \) is the Gaussian Curvature.

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

\[ \psi(\xi) = A(0)\xi(1 + \frac{1}{3}K\xi^2) \]  

[S3]

The patch on the parallel surface \( A(\xi) \) can be translated to an area on the pivotal surface \( A_n \), and \( \psi(\xi) \) can be translated to \( V_n \), the volume between the minimal surface, and the pivotal surface where \( \xi \) 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 \( <K> \), \( <A_n> \), \( <V_n> \) respectively.

Combining Equation S2 and Equation S3 gives

\[ \frac{<A_n>}{<V_n>} = \frac{1}{\xi} \left( \frac{1 + <K>\xi^2}{1 + \frac{1}{3}<K>\xi^2} \right) \]  

[S4]

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

\[ <K> = \frac{2\pi\chi}{\sigma_0 a^2} \]  

[S5]

The variation of \( \xi \) with water volume fraction, \( \phi_w \), is then determined by the following equation S6.

\[ \frac{<V_n>}{<V>} (1 - \phi_w) = 2\sigma_0 \left( \frac{\xi}{a} \right) + \frac{4}{3} \pi \chi \left( \frac{\xi}{a} \right)^3 \]  

[S6]

Combining Equations S4-6 and solving gives a relationship between the lattice parameter \( a \), water volume fraction \( \phi_w \) of the phase and the pivotal surface parameters \( A_n, V_n, V \) (Equation S7).
\[ a = \frac{<v_n>}{<A_n>(1 - \phi_w)} \left(-2\sigma + \frac{\frac{5}{2}\sigma^2}{\left(4\sigma^3 + 9\pi(1 - \phi_w)^2 \left(\frac{<v_n>}{V}\right)^2 + 3(1 - \phi_w) \left(\frac{<v_n>}{V}\right)\right) \sqrt{\pi\chi\left(8\sigma^3 + 9\pi(1 - \phi_w)^2 \left(\frac{<v_n>}{V}\right)^2\right)}\right)^{\frac{1}{3}} \]

\[ + 2\left(\frac{4\sigma^3 + 9\pi(1 - \phi_w)^2 \left(\frac{<v_n>}{V}\right)^2 + 3(1 - \phi_w) \left(\frac{<v_n>}{V}\right)\right) \pi\chi\left(8\sigma^3 + 9\pi(1 - \phi_w)^2 \left(\frac{<v_n>}{V}\right)^2\right)\right)^{\frac{1}{3}} \]

\[ \phi_w \] is the water volume fraction and can be calculated from the water content (wt % water) from Equation S8

\[ \phi_w = \frac{C_w}{C_w + (1 - C_w) \cdot \frac{\rho_w}{\rho_l}} \]  

[S8]

Where \( C_w \) is the water content (wt% water); \( \rho_w \) is the density of water; \( \rho_l \) 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\( \text{II}^G \) 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 \( \phi_n \) (\( \phi_n = \frac{v_n}{V} (1 - \phi_w) \)), to obtain Equation S9.\(^{3,5}\)

\[
S_n = a^2 \sum_{i=0}^{\infty} \sigma_i \phi_n^{2i} \quad \text{[S9]}
\]

Where \( S_n \) is the area of the pivotal surface, \( a \) is the lattice parameter, and the \( \sigma_i \) are given by: \( \sigma_0 = 3.0915; \sigma_1 = -1.3317; \sigma_2 = -0.19974; \sigma_3 = -0.80113 \).

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

\[
S_n = \frac{A_n a^3 (1 - \phi_w)}{2} \quad \text{[S10]}
\]

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

\[
\alpha = 2 \sum_{i=0}^{\infty} \frac{\sigma_i (\frac{v_n}{V} (1 - \phi_w))^{2i}}{(\frac{v_n}{V} (1 - \phi_w))} \quad \text{[S11]}
\]

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:
