**THE MEMBRANE SYSTEM OF THE CELL**

**PLASMA MEMBRANE**

The outer boundary of the cell is the plasma membrane, a continuous sheet of phospholipid molecules about 4-5 nm thick in which various proteins are embedded.

Some of these proteins serve as pumps and channels for transporting specific molecules into and out of the cell.

**ENDOPLASMIC RETICULUM**

Flattened sheets, sacs, and tubes of membrane extend through the cytoplasm of eukaryotic cells, enclosing a large intracellular space. The ER membrane is in structural continuity with the outer membrane of the nuclear envelope, and it specializes in synthesis and transport of lipids and membrane proteins.

The rough endoplasmic reticulum (rough ER) generally occurs as flattened sheets and is studded on its outer face with ribosomes engaged in protein synthesis.

The smooth endoplasmic reticulum (smooth ER) is generally more tubular and lacks attached ribosomes. It has a major function in lipid metabolism.

**GOLGI APPARATUS**

A system of stacked, membrane-bounded, flattened sacs involved in modifying, sorting, and packaging macromolecules for secretion or for delivery to other organelles.

Around the Golgi apparatus are numerous small membrane-bounded vesicles (50 nm and larger) that carry material between the Golgi apparatus and different compartments of the cell.

**LYSOSOMES**

Membrane-bounded vesicles that contain hydrolytic enzymes involved in intracellular digestions.

**PEROXISOMES**

Membrane-bounded vesicles containing oxidative enzymes that generate and destroy hydrogen peroxide.
Energetics of Phospholipid Self-Assembly

Cylindrical Micelles

What is the driving force for phospholipid self-assembly?
Spontaneous self-assembly is NOT driven by attraction between phospholipid molecules.

**Energy Units**

\[ k_B T_{\text{room}} = 1.38 \times 10^{-16} \text{erg} = 4 \times 10^{-4} \text{erg} = 4 \times 10^{-2} \text{kJ} \]

(physicist)

\[ (\text{chemist}) \]

\[ 1 \text{kJ/mole} = 1.04 \times 10^{-2} \text{eV/mole} = 1.6 \times 10^{-4} \text{eV} = 0.4 \text{kJ} \]

**In these units**

- **Covalent bonds**
  - \( \text{C} = \text{C} \) 140 kJ/mol
  - \( \text{C} = \text{C} \) 244 kJ/mol

- **vdW bond**
  - \( \text{CH}_3 \cdot \cdot \cdot \text{CH}_3 \) 3 kJ/mol

- **trans/gauche**
  - 5 kJ/mol

- **Hydrogen bond**
  - Water - water
  - Water - polyelectrolyte
  - Not water - hydrocarbon

Local order in H2O max, these bonding contacts.
Phospholipid self-assembly → soft, flexible, fluid-like structure

Forces that hold amphiphilic molecules together are **NOT due to strong covalent ionic bonds** but are due to much weaker VdW hydrophobic interaction hydrogen bonding screened electrostatic interactions

Environmental changes e.g. pH electrolyte conc

→ affect intramolecular forces colin aggregates

→ Δ size, shape of assembly

→ Δ aggregate interactions
"Hydrophobic effect" as the Main Driving Force.

Let's look at the entropic contributions to the "hydrophobic effect"

\[ F = E - TS \]
Obj: min free energy

Free energy can be min. in 2 ways:

1. ↑ binding (vE)
   typically dominates in solids

2. ↑ accessible configs. (vS)
   typically dominates in fluids

Entropic Picture:
When water sits next to an (interface) hydrophobic environment

→ partial freezing occurs
due to immobilization

→ ↓ in entropy
→ inc in free energy cost/area

* Water Structure @ heat Interfaces
  see Y.R. Shen; K. Eisenenthal
Why is it more immobilizing to sit next to hydrocarbons than next to polar groups (heads)?

\( \text{\Delta more free energy cost for water/hydrocarbon than water/heads interface} \)

When water sits against another material, the local order is reduced, compared that to the bulk.

\( \rightarrow \text{less bonding} \)

\( \rightarrow \text{again incur energy cost/unit area} \)

This is on top of the entropic effects!

\[
\sigma_{\text{water/air}} = 70 \text{erg/cm}^2 \sim 0.2 \text{kJT/Å}^2 \\
(30^\circ C)
\]

\[
\sigma_{\text{water/oil}} \sim 30 \text{erg/cm}^2 \sim 0.07 \text{kJT/Å}^2
\]

Use this to do some back of the envelope calculations to get a few of the order of magnitude of forces at hand.
A single phospholipid molecule is very insoluble!

\[ 40 \text{Å} \quad \rightarrow \quad 15 \text{Å} \quad \leftarrow \]

Hydrophobic area/molecule
\[ \approx 300 \text{Å}^2 \]

Energy cost in exposing tail portion to water
\[ \approx 300 \text{Å}^2 \times (0.07 \text{ kBT/Å}^2) \approx 21 \text{ kBT/molecule} \]

i.e. expect factor \( e^{-\Delta G/k_BT} \) in solubility

\[ e^{-21} \approx 10^{-10} \text{ Mole in typical phospholipid} \]

This forces phospholipid in water to aggregate in such a way as to shield tails from hydrophobic exposure to water.

One way to do this is to form a bilayer.

* Will discuss the exact shape formed later & the constraints for diff. structures.
Once a bilayer is formed, it's very difficult to switch a phospholipid molecule from one side to the other (unless there are edges/pores).

Area of head group
\[ \sim 175 \text{Å}^2 \]

Energy cost in expelling head group to hydrocarbon
\[ \sim 175 \text{Å}^2 (0.07 \text{ kcal/Å}^2) \]
\[ \sim 12 \text{ kcal} \]

By contrast, the energy cost of putting a single water molecule into the bilayer interior is roughly
\[ A \sim 4 \pi (1 \text{Å})^2 \sim 12 \text{Å}^2 \]
\[ \Delta E \sim 12 \text{Å}^2 (0.07 \text{ kcal/Å}^2) \sim \text{ kcal} \]

\[ \therefore \text{ water passes readily through membrane} \]

Cholesterol can also flip flop quite freely.
Edges of bilayer cost hydrophobic energy

\[ \lambda_{\text{edge}} = 8 \times 10^{-6} \text{ erg/cm} \]

This provides the "force" which acts to make bilayer sheets assemble into closed vesicular type of structures.

* However, if you can stabilize the edge with other surfactant
  → can form stable bilayer structures
  → used in NMR as a lipid mimicking environment
What happens when you start off pure water and slowly add lipid into it?

WATER - AMPHIPHILE AGGREGATION PHENOMENA

"Lytotropic Phases"

Generic Amphiphile - water structures

- **Single molecule**
  - only at low conc.
  - $10^{-10}$ M

- **Small n complexes**
  - anything which shields hydrocarbons from aqueous environment

- **micelles**
  - may or may not be spherical
  - relative size of head/tail
  - new length scale
  - micellar crystals
  - micellar liquid crystals

- **hexagonal (H)**
  - other linear phases
  - cylindrical micelle or dal objects
lamellar (L)

- hex a lamellar
- do 3 crystalline structure
- Plumber's nightmare

Cubic (Q)

- monolayer
- micellar
- linear

- bilayer
- bicontinuous

Some cubic (bicontinuous phases have been seen in biology)
Plus:

- Inverted versions of all the above
  - Micelles $\rightarrow$ Inverted micelles
  - Hexagonal (H) $\rightarrow$ Inverted hexagonal (H)

- Disordered versions of all the above
  - Hex $\rightarrow$ Spaghetti
  - Lamellar Cubic $\rightarrow$ Sponge
  - Micellar Crystal $\rightarrow$ Micellar fluid

* Read more about cubic phases
  See Sol Gruner's work
Phase Diagrams

Phospholipid phase diagrams remain incompletely known.

Basic sequences of phases determined geometrically by packing constraints. Preferred monolayer curvature.

The intermediate phases a, b, c, d are typically (but not always) cubic:

- **a**: packed micelles (or monolayer cubic)
- **b, c**: bilayer cubic, bicontinuous, sponge
- **d**: packed inverse micelles (or monolayer cubic)
These geometrical sequences show up in phase diagrams but are often cut off fluid phase (disordered)

\[ \text{freezing, crystalline phase} \]

\( \phi = \% \text{ amphiphile} \)

- CMC = critical micelle conc. when do micelles first form? (not a sharp line)
  \( 10^{-2}\text{M} \) for phospholipids

- 1\textsuperscript{o} coexistence (almost always) but it may be narrow

- Bulk amphiphile phase may be lamellar

- Phase separation w/ water-rich & amphiphile-rich may be broad

- Knowledge on phase diagram \( \rightarrow \) rather poor active area of research

* Phospholipids Handbook, ed. Centi (Dekker, NY, 1993)

* Chen & Physicochem Lipids 57 (1990) Special Issue
Thermodynamics of Self-Assembly

Wiley, NY

\[ \frac{1}{k_T} = \frac{k_1}{k_2} \]

- Number Activity
- Chemical Potential

\[ N, \quad X_1, \quad \mu_l \]

\( \mu \) for all identical molecules in a homogenous system,
how to be the same @ equil:

\[ \mu = \mu_1 = \mu_l^0 + kT \log X_1 \]

monomer

\[ = \mu_2 = \mu_l^0 + \frac{kT}{2} \log \frac{X_2}{2} \]

dimer

\[ = \mu_3 = \mu_l^0 + \frac{kT}{3} \log \frac{X_3}{3} \]

trimer

\[ \vdots \]

\[ = \mu_N = \mu_l^0 + \frac{kT}{N} \log \frac{X_N}{N} \]

N-mer

mean chem. potential
mean interaction free energy per molecule
Rate of association = $k_1 x_i N$
Rate of dissociation = $k_N \left( \frac{X_N}{N} \right)$

At equil,

Rate of associate = Rate of dissociation

$k_1 x_i N = k_N \left( \frac{X_N}{N} \right)$

$\therefore$ Equil const.

$K = \frac{k_1}{k_N}$

$= \left( \frac{X_N}{N} \right) \frac{1}{x_i}$

But $X_N = N \exp \left[ \frac{N}{kT} (\mu - \mu^0) \right]$

$x_i = \exp \left[ \frac{1}{kT} (\mu - \mu^0) \right]$

$\therefore K = \frac{\exp \left[ N \frac{\mu - \mu^0}{kT} \right]}{\exp \left[ CN \frac{\mu - \mu^0}{kT} \right]}$

$= \exp \left[ \frac{CN (\mu - \mu^0) / kT}{N} \right]$
For an $m$- and $N$-aggregates, we can write down their chem. potential @ equil:

\[
\mu^0 + \frac{\mu}{M} \log \frac{X_M}{M} = \mu^0 + \frac{kT}{N} \log \frac{X_N}{N}
\]

\[
N\mu^0 + kT \log \frac{X_M}{M} = N\mu^0 + \frac{N}{N} kT \log \frac{X_N}{N}
\]

\[
M(\mu^0 - \mu^0) + kT \log \frac{X_M}{M} = \frac{N}{N} kT \log \frac{X_N}{N}
\]

\[
\frac{X_N}{N} \exp \left[ M(\mu^0 - \mu^0)/kT \right] = \left( \frac{X_M}{M} \right)^{N/M}
\]

\[
\therefore X_N = N \left\{ \frac{X_M}{M} \exp \left[ M(\mu^0 - \mu^0)/kT \right] \right\}^{N/M}
\]

For $N = 1$

\[
X_N = N \left\{ x_1 \exp \left[ (\mu^0 - \mu^0)/kT \right] \right\}^N
\]

Conservation of materials

\[
C = X_1 + X_2 + \ldots = \frac{8M}{\sum X_N}
\]
Together, these eq's completely define the sys.

Note:
- C - cane.
- \(x_n\) - activity
- \(v_f\) - fraction or mol fraction
- Neither can be greater than 1
- Dilute limit - interaggregate interactions ignored

Conditions Necessary for the Formation of Aggregates
- If a diff. \(v_i\) cohesive energy \(x_i\) molecules
  in agg. + monomer state
- If molecule in diff. sized agg. experiences
  the same interaction

\[ x_n = N x_i, \quad n \quad \text{for } \mu_i = \mu_i^0 = \ldots = \mu_i^0 \]

Since \(x_i < 1\)
\[ x_n << 1 \]

For aggregation to take place

\[ \mu_i^0 \leq \mu_i \]

Possibilities:
1. \(\mu_i^0\) increases as \(N\) increases
2. \(\mu_i^0\) has a min.
Variation of $\mu_N^0$ with $N$ for different geometries

1. 1-D aggregates (rods)

$\mu_N = \alpha kT$

For a $N$-mer, total interaction energy

$\mu_N^0 = -(N-1)\alpha kT$

$\mu_N^0 = -(-\frac{1}{N})\alpha kT$

$\mu_N^0 = -\alpha kT + \frac{\alpha kT}{N}$

$\mu_{\infty} = \mu_{\infty}^0 + \frac{\alpha kT}{N}$

bulk energy in an infinite aggregate

$\lim_{N \to \infty} \mu_N^0 = \mu_{\infty}^0$

Similar expression can be obtained for rod-like uniaxial
2-D aggregates (discs, sheets)

\[ N \propto \pi R^2 \]
unbound molecules @ rim
\[ \propto 2\pi R \]
\[ \propto N^{1/2} \]

\[ \mu = \mu^0 + \frac{\alpha kT}{N^{1/2}} \]

3-D aggregates (spheres)

\[ N \propto \frac{4}{3} \pi R^3 \]
unbound molecules @ surface
\[ \propto 4\pi R^2 \]
\[ \propto N^{2/3} \]

\[ \mu = \mu^0 + \frac{\alpha kT}{N^{1/3}} \]
For a spherical aggregate of radius $R$ made up of monomers of volume $V$, e.g. alkanes in H$_2$O:

$$N = \left(\frac{4\pi R^3}{3}\right) \left(\frac{1}{V}\right)$$

Free energy = $N\mu^0 + 4\pi R^2 \sigma$

$$\Delta \mu^0 = \mu^0 + \frac{4\pi R^2 \sigma}{N}$$

$$= \mu^0 + \frac{4\pi \sigma \left(\frac{V}{4\pi}\right)^\frac{3}{2}}{N}$$

$$= \mu^0 + \frac{4\pi \sigma \left(\frac{3V}{4\pi}\right)^\frac{3}{2}}{N}$$

$$= \mu^0 + \frac{\alpha kT}{N^{1/3}}$$

$$\alpha kT = 4\pi \sigma \left(\frac{3V}{4\pi}\right)^\frac{3}{2}$$

$$\alpha = \frac{4\pi \sigma \left(\frac{3V}{4\pi}\right)^\frac{3}{2}}{kT}$$

$$r = \left(\frac{3V}{4\pi}\right)^\frac{1}{3} = \text{effective radius}$$
$\alpha > 0$

dep. on the strength of
the intermolecular interaction

In general, the interaction energy of the molecule for the simple structure

$$\mu_N = \mu_0 + \frac{\alpha kT}{N^p}$$

$P$ - dep. on the shape or dimensionality of the aggregates

?? What determines when aggregates form ??
Critical Micelle Concentration (CMC)

\[ X_N = N \left\{ X_i \exp \left[ \frac{(\mu_i^0 - \mu^0)}{kT} \right] \right\}^N \]

\[ = N \left\{ x_i \exp \left[ \frac{a kT - \frac{a kT}{N^f}}{kT} \right] \right\}^N \]

\[ = N \left\{ x_i \exp \left[ \left( 1 - \frac{1}{N^f} \right) a \right] \right\}^N \]

\[ = N \left\{ x_i e^{a} \right\}^N \]

For low conc \( x_1 \) \& \( x_i e^{a} \ll 1 \)

\( x_1 > x_2 > x_3 \) for all \( a \)

\( \rightarrow \) isolated monomers : the preferred state

\( \rightarrow x_i \ll C \)

As \( x_i e^{a} \rightarrow 1 \) or \( x_i \rightarrow e^{-a} \)

it cannot \( \uparrow \) anymore ! \( X_N \) has to be \( 1 \)

\( (X_i)_{\text{crit}} = \text{critical micelle conc.} \)

\( = \text{critical aggregation conc.} \)

\( x_i > (X_i)_{\text{crit.}} \rightarrow \text{micelles form} \)

\( \text{CMC} = \exp \left[ \frac{-(\mu_i^0 - \mu^0)}{kT} \right] = e^{-a} \) for all \( p \)
How many monomers in a micelle?

Exact # dep. on length of hydrocarbon chain

\[ RN(CH_3)_2^+ \text{ CH}_3\text{COO}^- \]

<table>
<thead>
<tr>
<th># C in R</th>
<th>N in aggregate</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>24</td>
</tr>
<tr>
<td>15</td>
<td>130</td>
</tr>
</tbody>
</table>
Geometric Packing Considerations

Depends on

1. Optimal area, $A_o$
2. Vol. of hydrocarbon chains, $V$
3. Max effective chain length, $l_c$

(for fluid, in comp. state)

\[ l_c \leq l_{max} \]

\[ V \leq (0.154 + 0.126n) \text{ mm} \]

\[ V \approx (27.4 + 26.9n) \times 10^{-3} \text{ nm}^3 \]

For large $n$

\[ \frac{V}{l_c} \leq 0.21 \text{ nm}^2 \]

\[ \leq \text{ min x-sectional area of a hydrocarbon chain} \]

If 1, 2, and 3 are known, structure formed can be determined.
For same $a^0$, $\mu^0$ may be the same for diff. structures.

Entropy will favor the structure with smallest config. # ($N=M$).

Larger structure $\rightarrow$ entropically unfavorable.
Smaller structure $\rightarrow$ face $a > a_0$.
Energetically unfavorable

Packing parameter or shape factor:

$$\frac{V}{\text{asle}}$$

determines the structure formed.
Spherical Micelles

\[ M = \frac{4\pi R^2}{a_0} \]
\[
\text{but } V = \frac{a_0 R}{3}
\]
\[ M = \frac{4\pi R^3}{3V} \]
\[
\frac{4\pi R^2}{a_0}, \quad \frac{3V}{4\pi R^3} = 1 \quad \text{max.}
\]
\[ \therefore \frac{V}{a_0 R} = \frac{1}{3} \]
\[ \therefore \frac{V}{a_0 l_c} < \frac{1}{3} \]
\[ l_c < R \]

e.g. Sodium dodecyl Sulphate (SDS)

exp. \( M = 74; \ n = 12 \)
\[ \therefore V = (27.4 + 26.9 \times 12) \times 10^{-3} = 0.3502 \text{ nm}^3 \]
\[ a_0 = 0.57 \text{ nm}^3 \]
\[ R = 1.84 \text{ nm} \]
But \( l_c = 1.67 \text{ nm} \)
\[ \therefore \frac{V}{a_0 l_c} \approx 0.37 \rightarrow \text{non-spherical micelles.} \]
Cylindrical Micelles

\[ \frac{1}{3} < \frac{V}{a_0 \cdot c} < \frac{1}{2} \]

- \( \text{eg. addition of salt, screening headgroup repulsion} \)
  - Already shown (\( p=1 \))
    - \( \ast \) large
    - \( \ast \) polydisperse
    - \( \ast \) agg # \( \propto \sqrt{c} \)
- Special prop. due to ‘end effects’

\[ \frac{a}{2} c \leq 1 \rightarrow a_{\text{cap}} > a_0 \]

Unfavorable cap configuration determines magnitude of interaction term \( \alpha \)

- \( \text{eg. } \alpha \uparrow \text{ as } a_0 \uparrow \)

Recall \( \langle N \rangle = 2NCE^\alpha \)

- Changes are T., pH, Ionic Strength
  - \( \text{eg. SDS in 0.6 M NaCl} \quad \text{agg #} \sim 1000 \)
  - \( \text{vs. water} \quad \text{agg #} \sim 60 \)
Bilayers

$$\frac{V}{\sigma_0 \ell_c} \approx 1$$

Same as $\sigma \ell_c$, $V$ has to double for this requirement to hold.

→ Bilayers are formed by lipids that have 2 tails.

Chain doubling affects aggregation properties, both static and dynamic:

1. $V$ CMC (↑: ↑ hydrophobicity) + dynamic
   - Micelles: $10^{-2} \sim 10^{-5} \text{M}$
   - Bilayers: $10^{-6} \sim 10^{-10} \text{M}$

2. ↑ residence time, $\tau_R$, $\tau_R$/in agg.
   - Related to activation energy, $\Delta E$,
   - For molecules to escape from agg. + back.

   With $\tau_0 \equiv$ collision time,

   $\text{Prob} \propto e^{-\Delta E/kT}$

   $$\tau_R \leq \frac{\tau_0}{e^{-\Delta E/kT}}$$

   $\Delta E \equiv (\mu_i - \mu_0)$

   $\tau_{R(\text{micelle})} \sim 10^{-4} \text{s}$

   $\tau_{R(\text{bilayer})} \sim 10^{+4.5} \text{s}$
CMC decreases with chain length.

Exchange rate for each add of 2 CH₂ groups (to double tail) \( \downarrow 4-10 \times \)

③ Flip-flop - diffusive exchange

\[ T_{ff} \sim 10^2 - 10^5 \, s \]

**Vesicles**

- Formation of closed spherical structures
- Delimits edge energy for disk-like structures
- Entropically favorable
  - finite vs. infinite agg. #

As long as min area can be maintained

\[ \frac{1}{2} < \frac{V}{\alpha \, \text{ole}} < 1 \]

Formation of a curved surface leads to truncated cone geometry
Critical Radius

\[ R_{c} = \frac{\alpha_{c}}{6\left(1 - \frac{\alpha_{c}}{\alpha_{0}}\right)} \]

Smallest radius \( R \) at which the headgroup area \( \alpha_{c} \) is not allowed to exceed \( \alpha_{0} \):

- \( R < R_{c} \) \( \Rightarrow \alpha_{c} < \alpha_{0} \)
- \( R > R_{c} \) \( \Rightarrow \) entropically unfavorable

At \( R = R_{c} \):

- Bilayer thickness \( \vartheta \)
- Approximate number of particles \( N \)

\[ \begin{align*}
\text{approx. } N & \approx 4\pi [R_{c}^2 + (R_{c} - t)^2]^{1/2} / \alpha_{0} \\
\text{approx. } R_{c} & \approx 0.77 \text{nm} \\
\text{approx. } R_{c} & \approx 0.77 \text{nm} \\
\text{approx. } \vartheta & \approx 0.85 \text{nm} \\
\text{approx. } t & \approx 3.0 \text{nm}
\end{align*} \]

\( R_{c} \approx 11 \text{nm} \)

\( N \approx 3000 \)

\( \frac{\vartheta}{\vartheta_{0}/\alpha_{0}} \approx 0.85 \Rightarrow \text{vesicle} \)
Inverted Structures

\[ \frac{V}{\alpha \lambda c} > 1 \]

Small optimal area
bulky polysaturated chains (large \( \alpha \), small \( \lambda c \))

\[ K_c = \frac{\lambda c}{1 - V/\alpha \lambda c} \]

\(< 0\)

inverted structures resulted.
Factors Affecting Changes from One Structure to Another

1. Headgroup
   - Small head \(\rightarrow\) large vesicle
   - Less curved bilayers
   - Inverted micelles
   - \(\downarrow\) effective head size \(\rightarrow\) Ca^{2+}
   - pH 7

2. Chains
   - Branching \(\rightarrow\) \(\downarrow l_c, \uparrow v\)
   - \(\rightarrow\) large vesicles
   - Inverted structures

3. Temperature
   - \(T\uparrow\) \(\rightarrow\) trans-gauche, Denaturing
   - \(\downarrow l_c\)
   - \(\rightarrow\) \(\uparrow V/v ld_c\)
   - \(T\uparrow\) can \(\Delta a_o\) too
   - Usu. \(A_o\uparrow\) (more hydrophobic heads)
   - \(\rightarrow\) \(\downarrow V/v ld_c\)
   - Nonionic micelle \(\rightarrow\) grows
   - Ioniz \(\rightarrow\) shrinks
   - \(2\alpha\) \(\rightarrow\) \(\times \Delta E/T\)
<table>
<thead>
<tr>
<th>Lipid</th>
<th>Critical packing parameter $w/a_0/l_c$</th>
<th>Critical packing shape</th>
<th>Structures formed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single-chained lipids (surfactants) with large head-group areas: SDS in low salt</td>
<td>$&lt; 1/3$</td>
<td>Cone</td>
<td>Spherical micelles</td>
</tr>
<tr>
<td>Single-chained lipids with small head-group areas: SDS and CTAB in high salt, nonionic lipids</td>
<td>$1/3-1/2$</td>
<td>Truncated cone</td>
<td>Cylindrical micelles</td>
</tr>
<tr>
<td>Double-chained lipids with large head-group areas, fluid chains: Phosphatidyl choline (lecithin), phosphatidyl serine, phosphatidyl glycerol, phosphatidyl inositol, phosphatidic acid, sphingomyelin, DGDG*; dihexadecyl phosphate, dialkyl dimethyl ammonium salts</td>
<td>$1/2-1$</td>
<td>Truncated cone</td>
<td>Flexible bilayers, vesicles</td>
</tr>
<tr>
<td>Double-chained lipids with small head-group areas, anionic lipids in high salt, saturated frozen chains: phosphatidyl ethanolamine, phosphatidyl serine + Ca$^{2+}$</td>
<td>$\sim 1$</td>
<td>Cylinder</td>
<td>Planar bilayers</td>
</tr>
<tr>
<td>Double-chained lipids with small head-group areas, nonionic lipids, poly (cis) unsaturated chains, high T: unsat, phosphatidyl ethanolamine, cardiolipin + Ca$^{2+}$ phosphatidic acid + Ca$^{2+}$ cholesterol, MGDG*</td>
<td>$&gt; 1$</td>
<td>Inverted truncated cone or wedge</td>
<td>Inverted micelles</td>
</tr>
</tbody>
</table>

*DGDC, digalactosyl diglyceride, diglucosyl diglyceride.

*MGDG, monogalactosyl diglyceride, monoglucosyl diglyceride.
Remarkable, chiral patterns are seen if about 2% cholesterol is present in a monolayer of $S$-dipalmitoylphosphatidylcholine and the film is compressed to the plateau region (e.g., as in Fig. IV-37). One such pattern is shown in Fig. IV-39 (284). The behavior has been modeled theoretically in terms of a line tension between the crystalline and liquid phases (284).

Other lipid-containing systems that have been studied include mixed films of dioleoylphosphatidylcholine with retinal (285) and with cytochrome $c$ (including surface potential and ellipsometric measurements) (286) and of lipid films with porphyrins (fluorescence studies) (287). Monolayer studies have also been reported on other membrane constituents such as valine-gramicidin A and Valinomycin (288). Finally, a bridged porphyrin, mesoporphyrin II, a somewhat spherical molecule, showed monolayer $\pi-\sigma$ behavior surprisingly like that of the long-chain fatty acids (289).

C. Films at the Oil-Water Interface

As has been noted, much of the interest in films of proteins, steroids, lipids, and so on, has a biological background. While studies at the air-water interface have been instructive, the natural systems approximate more closely to a water-oil interface. A fair amount of work has therefore been reported for such interfaces in spite of the greater experimental difficulties.

Protein monolayers tend to be expanded relative to those at the air-water interface (290). Davies (291) studied hemoglobin, serum albumin, gliad and synthetic polypeptide polymers at the water-petroleum ether interface with the view of determining the behavior of the biologically important NH$_2$ groups and concluded that on compression they were forced into the phase.

The $\pi-\sigma$ data for such films still fit Eq. IV-61, but with a larger $z$ value indicating more flexibility in the chain. Presumably this is because the presence of the oil phase reduces cohesion between the hydrophobic side chains of the protein molecule.

Stigter and Dill (292) studied phospholipid monolayers at the n-heptane-water interface and were able to treat the second and third virial coefficients (see Eq. IV-60) in terms of electrostatic, including dipole, interactions. Higher film pressures, Pethica and co-workers (292a) observed quasi-first-order phase transitions, that is, a much flatter plateau region than shown...
Figure 3. Fluorescence microscope images of methyl hexadecanoate along the L.E - LC phase boundary. (a) 28 C; (b) 20 C. The bars represent 100 μm. Note the sixfold changes in curvature that appear at 27 C.

Figure 4. Fluorescence microscope images with polarized excitation. The bars represent 100 μm. (a) Methyl octadecanoate at 31 C; (b) methyl eicosanoate at 20 C. The octadecanoate domains are chiral; those in the eicosanoate are achiral.
FIG. 1. Schematic pressure-temperature (σ-T) phase diagram showing several of the monolayer phases that have been identified in fatty acids and their esters. The relative locations of the gas (G), liquid-expanded (L₁), and superliquid phases (LS) are much the same for many substances. The locations of the other phases and the positions of the boundaries between them are more variable and less well known. The inset shows the orientation of the molecular tilt azimuth with respect to the local sixfold structure of the head groups that exists in the three tilted hexatic phases L₁, L₂, and L₂*.

director points toward nearest neighbors in the L₂ phase, toward next-nearest neighbors in the L₂* phase, and along an intermediate direction in the L₁ phase. In the language of smectic liquid crystals, the tilted LC phases are the analogs of, respectively, the smectic-I, -F, and -L phases (we will use this latter notation). The fact that the surfactant liquid crystals appear to be hexatics is somewhat surprising since tilted hexatics are less common in the phase behavior of D = 3 liquid crystals. On the other hand, the nematic phase, which is quite common in D = 3 liquid crystals, appears to be absent in the surfactant films studied to date.

Liquid crystals in D = 3 are birefringent and can be characterized visually by their striking multicolored textures when viewed between polarizers; the textures reflect the spatial variation of the local optical axis of the material. This spatial variation may be due to metastable “defects,” which for topological reasons cannot decay, or, for finite systems, it may be imposed by boundary conditions at the sample boundary. Textures are also very useful as a quick diagnostic for the type of liquid crystal involved. Recent studies of monolayers by polarized fluorescence [7] and Brewster-angle reflection [8,9] have shown that the spatial variation of the c director can be observed and demonstrated that LC phases of surfactant monolayers also exhibit textures; see Fig. 2.

At first sight, it would appear natural to expect that LC-phase textures should be similar to those of the analogous D = 3 smectic phases for achiral molecules (the surfactant molecules used were generally achiral). The most striking texture of the D = 3 phases is a fivefold star-shaped object [2]. The appearance of stars in tilted hexatics can be readily explained by allowing the c director to couple to the local orientation of the six hexatic crystallographic axes (see below). LC phases have indeed been found to exhibit star textures very similar to those of the free-standing tilted smectic hexatic films, but a large variety of other textures has been found as well. For example, the “ground state” of the LC phase for some fatty acids is a stripe texture consisting of straight or kinked defect lines [10]. The mesoscopic studies thus suggest that the analogy between surfactant monolayers and the D = 3 tilted-hexatic liquid crystals may not be complete since in the latter the ground state is believed to be uniform.

B. Droplet textures

The spatial variation of the optical axis of a texture reflects an inhomogeneous structure of the underlying order parameter. The order parameter of an LC phase is rather complex: it is a combination of the c director and

FIG. 2. Images of droplet textures. The droplets are surrounded by the liquid expanded phase, which is isotropic. (a) Polarized fluorescence microscope image of a star defect in a monolayer of methyl octadecanoate. (b) Brewster-angle microscope image of a boojum in a monolayer of pentadecanoic acid (courtesy J. Meunier).
the hexatic order parameter. We characterize the hexatic order by the angle $\theta$ made by the six crystallographic axes with a fixed axis, say, the $x$ axis (see Fig. 3). This "bond-angle" field $\theta(x)$ can, like $\varepsilon(x)$, vary across the sample. Obviously, $\theta(x)$ is defined only modulo 60° so the LC free energy must be invariant under rotations by multiples of 60°. It is the experience in $D = 3$ systems that complex order parameters produce complex textural patterns and, as mentioned, a bewildering variety of textures has indeed been observed in monolayers. The question now is whether we can hope to carry out a program of texture classification in surfactant monolayers in the same way as has been done for $D = 3$ liquid crystals [11].

In this paper we will address this issue only for the simplest possible case, namely, that of a $D = 2$ LC droplet inside a LE matrix. In such a confined geometry, the number of allowed textures should be severely reduced by the boundary constraints imposed on both the $\varepsilon(x)$ and $\theta(x)$ fields at the LE-LC interface because they raise the energy cost of adding metastable topological defects. Electrostatic repulsions inhibit the coalescence of LC droplets and their sizes are therefore generally only of order 100 μm; their shapes usually vary between circular to (rounded) hexagonal.

Coexistence droplets in ester monolayers show a range of textures; some common ones are shown in Fig. 4. As one moves along the LE-LC coexistence curve, reversible changes are observed in both the texture and the droplet shape. On the basis of these relaxation processes, it is reasonable to assume that the observed textures represent a local equilibrium of the free energy rather than a frozen, or pinned, configuration determined entirely by the preparation history of the drops. The fluorescence data on the esters also reveal that $\varepsilon(x)$ is fairly strongly anchored along the normal to the LE-LC interface. The boundary condition on the bond-angle field (if any) is not known since the $\theta(x)$ field cannot be visualized by the fluorescence studies. The observed textures are often based on the sixfold hexagonal "basic motif" shown in Fig. 4(a). The origin of the basic motif is easily understood if we assume that the hexatic degree of freedom is relatively stiff and thus spatially uniform across the drop.

In each of the six sectors of the hexagon, the in-plane director is also uniform and locked to the bond-angle field with the relative angle between them assuming the equilibrium value appropriate for the LC phase in question. At the boundary between adjacent sectors, $\varepsilon(x)$ makes a rapid rotation of 60° to flip from one of the six hexatic directions to the next ("60° wall"). On the other hand, coexistence droplets of fatty acid monolayers have textures with no sharp boundaries but rather a smoothly varying $c$ director. Understanding the origin of the different phenomenology of ester surfactants and fatty acid surfactants is important for learning how to interpret the observed textures.

If the droplet shape is a perfect hexagon, then the basic motif naturally satisfies normal boundary conditions for the $c$ director at the LE-LC interface. In this view, hexagonal droplet shapes would be a consequence of the normal boundary conditions on the molecular tail rather than the direct influence of the hexatic order on the LE-LC interface. This is confirmed by the fact that in the high-pressure LS phase, where the molecules are perpendicular to the air-water interface, the droplets are not hexagonal even though the phase is believed to be hexatic [7]. It is important for the following to note that the strength of the boundary conditions on the $c$ director is, in reality, limited. As shown in Fig. 4(b), experiments also show the existence of circular drops with a hexagonal interior structure, which could only satisfy normal boundary conditions by distorting the textural uniformity inside the six sectors, which does not appear to be the case. As will be discussed below, a circular shape is actually a natural variation of the basic motif if we allow for an increase of the LE-LC line tension with respect to that of a 60° wall.

The basic motif is closely related to the five-armed star-shaped defects observed both in the LC phase of materials such as pentadecanoic acid away from the coexistence line as well as in freely suspended films of tilted smectic hexatics. We can crudely think of the basic motif as a stable star-type defect imposed by the LE-LC phase boundary. The difference

**FIG. 3.** Definition of the bond angle $\theta$, the tilt angle $\varphi$, and the director $c$.

**FIG. 4.** Droplet textures for hexatic phases. The lines indicate the orientation of the molecular tilt azimuth within each domain and the shading gives an impression of the contrast that would be observed in an image obtained by polarized fluorescence microscopy.
Textures in a chiral smectic liquid-crystal film

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(Received 10 March 1986)

Freely suspended liquid-crystal films of the smectic-I phase of HOBACPC \([R(\rightarrow)\) hexyloxybenzylidene \(p'\)-amino-2-chloropropyl cinnamate] display distinctive stripe and droplet textures. We derive these patterns from a Landau expansion of the free energy using a vector order parameter. Strong pinning boundary conditions lead to boojums in the droplets and stable defect lines between the stripes. The boojum is a two-dimensional version of its namesake in superfluid \(^3\)He-\(\Lambda\). The surface defect in the boojum is expelled from the smectic-I droplet in order to lower the internal gradient energy, leaving a defect-free texture. The expulsion distance and the width of the stripes are calculated in terms of the elastic constants.

I. INTRODUCTION

Smectic liquid crystals, in which the molecules arrange themselves in parallel layers, can be drawn into stable freely suspended films only a few molecular layers thick.\(^1\)-\(^4\) In the tilted smectic phases, such as SmC and SmI, the molecular optical axis \(\hat{a}\) lies at an angle to the layer normal (see Fig. 1). The direction of the projection \(\hat{c}\) of the molecular axis in the plane of the film can be observed by polarized reflection microscopy. Basically, if the direction of polarization of incident light is parallel or perpendicular to \(\hat{c}\), then the polarization is unchanged upon reflection, whereas if the direction of polarization of the incident beam is at some other angle, the polarization is rotated. When viewed through crossed polarizers, those regions of the film with \(\hat{c}\) parallel to either of the polarizers appear dark. These dark fringes are known as schliren lines.\(^5\) Defects in the liquid crystal show up as discontinuities or points of convergence of schliren lines.

Distinctive schliren patterns have been observed by Clark, Van Winkle, and Muzny\(^6\) in freely suspended films of HOBACPC \([R(\rightarrow)\) hexyloxybenzylidene \(p'\)-amino-2-chloropropyl cinnamate], a chiral liquid crystal which forms ferroelectric phases of SmC and SmI. Both SmC and SmI are tilted phases; while the nature of the ordering in these phases is still under investigation,\(^7\) SmC is known to have only short-range positional order within layers, while SmI has a more pronounced hexagonal order and more translational order than does SmC. In both cases there exists orientational order between layers. On cooling a SmC film through 55°C small roughly circular domains of SmI nucleate. The SmI droplets drift away from their nucleation sites and grow into the SmC. The droplets are characterized by one to three straight schliren lines which appear to originate at a point off the edge of the droplet. (See Fig. 2.) The schliren lines lie at 45° to one another. In circular droplets, relatively free from the distortions caused by contact with neighboring

![Fig. 1. Schematic of the experiment. The smectic film lies in the x-y plane. The film is viewed by reflection between crossed polarizers \(P_1\) and \(P_2\). The molecular optical axis is \(\hat{a}\)—the molecule shown lies in the y-z plane. The order parameter \(\hat{c}\) points towards the tops of the tilted molecules, and lies in the x-y plane. Consequently, when the film is viewed from below, the order parameter \(\hat{c}\) is the reverse of \(\hat{c}\).](image1)

![Fig. 2. Polarized reflection micrograph of the droplet texture. The polarization axes are parallel to the edges of the picture. The diameter of the illuminated region is roughly 0.24 cm. Photo courtesy of N. A. Clark, D. H. Van Winkle, and C. Muzny.](image2)
A. Conclusions

We describe the smectic film by a unit vector order parameter \( \hat{\xi} \). There are two contributions to the free energy of the film—bulk terms involving integrals of gradients of \( \hat{\xi} \) over the area of the system, and surface terms involving line integrals around the boundary of the system. In a system of size \( R \) the gradients of the order parameter scale as \( 1/R \). Since the bulk free-energy density is quadratic in the gradients, the total bulk free energy (integrated

Indeed a minimum of the free energy is achieved far the defect is expelled from the droplet.

The strong boundary conditions are also responsible for the presence of stripes in the film. Each defect-line carries a positive free energy \( J_0 \) per unit length, but because the boundary condition can be satisfied along the sides of the defect lines, the net free energy of the system may be negative. A negative defect energy does not lead to an infinite density of defect lines, however. In order to satisfy the boundary condition at both sides of a stripe, the order parameter must rotate through 180° between defect lines, so narrow stripes entail large gradient energy. The balance between gradient energies, surface energies, and defect core energies leads to a finite nonzero stripe width. This width is calculated in Sec. III A.

II. FORM OF THE FREE ENERGY

A. The order parameter

Let the smectic film lie in the \( x-y \) plane. At each point \( (x,y) \) in the film denote the local molecular axis of anisotropy by \( \hat{n} \), averaged over thermal motions and depth of the film. It is convenient to visualize \( \hat{n} \) as the long axis of the molecules, although this does not necessarily coincide with the optical anisotropy axis. Assuming that the molecules are effectively symmetrical in detail, there is no distinction between \( \hat{n} \) and \( -\hat{n} \), so we define the order parameter as \( \hat{\xi} \), a unit-vector order parameter \( \hat{\xi}(x,y) \), or, equivalently, an angle \( \xi(x,y) \), where \( \hat{\xi} = \hat{x} \cos \phi + \hat{y} \sin \phi \). \( \hat{\xi} \) points in the projection of \( \hat{n} \) in the \( x-y \) plane, as shown in Fig. 3.

HOBACPC has ferroelectric properties which lead to non-local terms in the free energy that are found experimentally to be important. Dipole interactions between benzyldiene-$p'$-amino-2-iodobenzoic acid molecules are similar to HOBACPC but with a higher degree of ionic impurities. Although the chemistry of HOBACPC is stronger than that of HOBACPC, we can also neglect these long-range interactions.

B. Symmetry

The free energy of the system is given by

$$F[\hat{e}] = \int \int dx \, dy \, F$$

where $F_{\text{defect}}$ is the free energy density $F$ is a function of the spatial coordinates and must be transformations which include rotations about the $\hat{x}$ or $\hat{y}$ axes, and translations of Chiral molecules are not stable and only if the liquid crystal is in a state of chiral order under reflections through the $\hat{z}$ axis.

The free-energy density includes bulk and surface terms. By minimizing the free energy over the whole system, we can determine the nature of the divergences and other terms that contribute to the free energy.

The bulk gradient terms in a Landau-Ginsburg free energy functional are the most important term in the system. A simple calculation shows that these terms represent the sum of all contributions to the free energy that arise from the bulk order parameter $\hat{e}$, which is a function of the spatial coordinates $x$ and $y$. The terms in this functional are given by

$$F[\hat{e}] = \int \int dx \, dy \, F$$

where $F$ is a function of the spatial coordinates and must be transformations which include rotations about the $\hat{x}$ or $\hat{y}$ axes, and translations of Chiral molecules are not stable and only if the liquid crystal is in a state of chiral order under reflections through the $\hat{z}$ axis.
DMPC / DChol

homogeneous

2-phase coexistence

\( \frac{\Pi}{\Pi_c} \)

\( x_1 \)

Paper3: Figure 1
PA + 20 wt% SP-B 1-25 at zero surface pressure
Presence of Stripe Phases in both PA/SP-B 1-25 and Fluorescein SP-B 1-25 Films
PATTERN FORMATION

• diverse set of physical, chemical, and biological systems exhibits macroscopic pattern and texture
  e.g. thin films of type I superconductors, ferrofluids, ferromagnetic garnets, chemical reaction-diffusion systems ...

• two partially incompatible species

• common structural features

• characteristic widths

• modulated by external parameters
Pattern Formation by Interacting Chemical Fronts
Lee, McCormick, Ouyang & Swinney
Science 261, 192 (93)
"Labyrinthine Pattern Formation in Magnetic Fluids"
Dickstein, Erreaulli, Goldstein, Jackson, Langer

Science, 261, 1012 (93)
MOTIVATION

Circular liquid monolayer domain

Stripe pattern

- Circular domains become unstable –
  under what conditions?
  turn into what shapes?
  any route?

- Quantitative understanding –
  model based on competing interactions?

- Experimentally observable?
LINE TENSION VS ELECTROSTATICS

idealization:
2 dimensional sheet of mobile dipoles

\( \lambda \) (line tension between two phases)
\[ \mu \] (dipole density in the phases)
\[ \Delta \] (next neighbor cutoff)

Equilibrium shapes: depend only on electrostatic and interfacial effects

Dynamics: affected by viscous coupling to sub- and super-phase.
Energetics of Lipid Domains

\[ F = F_{\text{el}} + F_{\text{ad}} \leftarrow \text{line tension energy} \]

\[ \text{domain shape-dep.} \]

\[ \text{electrostatic energy} \]

Energy of the dipole-dipole interaction in a 2D domain of area \( A \)

\[ \text{For two elements of area } dA + dA', \]

\[ \text{Energy of interaction } = \frac{\mu^2 dA dA'}{\rho^3} \]

\[ (F-F') \text{ is dist. } \gamma \text{ of elements.} \]

\[ \rho^2 = (F-F')^2 + \Delta^2 \]

\[ \text{cutoff} \]
Energy of dipole interaction

\[ E_A = \frac{1}{2} \int \int \int \frac{\mu^2 \text{d}A \text{d}A'}{\rho^3} \]

avoid double counting

Another way to look at it

Imagine A is surrounded by domain B that extends out to \( \infty \).

Let \( E \) be the energy per unit area of an infinite 2-D system (domain A plus B).

- \( A \) be the area of A
- \( B \) be the area of B

Total energy (infinite)

\[ \Sigma A + \Sigma B = E_A + E_B + \frac{\mu^2}{2} \int \int \frac{\text{d}A \text{d}B}{\rho^3} \]

\[ + \frac{\mu^2}{4} \int \int \int \frac{\text{dB} \text{d}A}{\rho^3} \]
\[
\rho = \rho_0 \cdot \frac{1}{\rho^n}
\]
\[
\frac{\partial \rho}{\partial x} + \frac{\partial \rho}{\partial y} = \frac{\partial \rho}{\partial x} \left( \frac{\partial \rho}{\partial x} + \frac{\partial \rho}{\partial y} \right) + \frac{\partial \rho}{\partial y} \left( \frac{\partial \rho}{\partial x} + \frac{\partial \rho}{\partial y} \right)
\]
\[
\frac{\partial \rho}{\partial x} + \frac{\partial \rho}{\partial y} = -\frac{1}{\rho} - \frac{\rho^2}{\rho^3}
\]
\[
\frac{\partial \rho}{\partial x} + \frac{\partial \rho}{\partial y} = -1 + \frac{\rho^2}{\rho^3}
\]
\[
\frac{\partial \rho}{\partial \rho} = n(n+1) \frac{1}{\rho^{n+2}}
\]
\[
\frac{\partial ^2 \rho}{\partial x^2} + \frac{\partial ^2 \rho}{\partial y^2} = -n^2 \frac{1}{\rho^{n+2}} + n(n+2) \frac{\rho^2}{\rho^{n+4}}
\]
\[
\int_A \int_B \frac{1}{\rho^{n+2}} \, dA \, dB' = -\iiint \frac{1}{\rho^n} \, d\tau \cdot d\tau'
\]
\[
+ \frac{(n+2)}{n} \iiint \int_A \int_B \frac{1}{\rho^{n+4}} \, dA \, dB'
\]
\[
\text{Green's Eqn}
\]
\[
\int_A \int_B \frac{1}{\rho^3} \, dA \, dB' = -\iiint \frac{1}{\rho} \, d\tau \cdot d\tau' + C
\]
Line integral around outer as perimeter of B is then neglected

$$\frac{1}{\rho} \to 0$$

When inner perimeter of B' is brought into contact with domain A

By convention the double line integrals from Green's Theorem are in opp. dir.

When B' is brought to A, it's convenient to let the 2 line integrals be in the same dir.

$$E_A = \varepsilon A - \frac{M^2}{\varepsilon} \int \int dF \cdot dF'$$

Related to ferromagnetic fluid calculations
What is the energy of domain $A$ in the absence of $B$?

$$E_A = E_A - \frac{M^2}{\rho} \iiint dA dB$$

Evaluate using Green's Theorem.

$A(x,y)$, $B(x',y')$, $P \neq 0 \Rightarrow f(x,y)$

For closed curves $\Gamma$, $A$

$$\oint \frac{\partial f}{\partial x} + \frac{\partial g}{\partial y} \, dx = \int P \, dx + Q \, dy$$

If $P, Q \Rightarrow f(x', y', y')$

$$\iiint \left( \frac{\partial g}{\partial x} - \frac{\partial P}{\partial y} \right) \, dx \, dy \, dz$$

$B' \, A'$

$$= \iiint P \, dx \, dx' + Q \, dy \, dy'$$
MODEL: LINE TENSION VS ELECTROSTATIC REPULSION

Free Energy

\[ F = F_{el} + F_{\lambda} \]

\[ F_{el} = \frac{\mu^2}{2} \iint \frac{dA \cdot dA'}{\rho^3} = -\frac{\mu^2}{2} \iiint \frac{d\vec{r} \cdot d\vec{r}'}{\rho} + C \]

\[ F_{\lambda} = \oint \lambda \, d\vec{r} \]

\[ \rho^2 = |\vec{r} - \vec{r}'|^2 + \Delta^2 \]

Circular domain of radius \( R \)

\[ F = 2\pi R \left( \lambda - \mu^2 \ln \frac{e^2 \Delta}{8R} \right) \]

Equilibrium radius

\[ R_{eq} = \frac{e^3 \Delta}{8} \exp \left( \frac{\lambda}{\mu^2} \right) \]
INSTABILITY OF A CIRCULAR DOMAIN

Energy associated with a circular domain with $n$-fold distortion

$$F_n = -\frac{\pi\mu^2 r_n^2}{2R_c} \left[ n^2 + \sum_{q=1}^{n+1} a_q L_q + \frac{n^2 - 1}{2} V(x) \right] + \frac{\pi\lambda r_n^2}{2R_c} \left( n^2 - 1 \right)$$
HARMONIC SHAPE TRANSITIONS

\[ R_n = \frac{\Delta}{8} e^{Z_n} \exp\left(\frac{\lambda}{\mu^2}\right) = e^{(Z_n-3)} \Re_{eq} \]

\[ Z_n = -\left[ n^2 + \sum_{q=1}^{n+1} a_q L_q \right] \left/ \left[ n^2 - 1 \right] \right. \]

\[ L_{n+1} = \frac{1}{2n+1} \left[ 4nL_n - (2n-1)L_{n-1} \right] \]

\[ a_q(n) = \begin{cases} 0.75 + (n-q) & \text{for } q = 1 \ldots n-2 \\ n-q & \text{for } q = n-1 \\ -0.5[n(n-1)+0.25]+1 & \text{for } q = n \\ 0.5 & \text{for } q = n+1 \end{cases} \]
HARMONIC SHAPE TRANSITIONS

\[ R_n = \frac{\Delta}{8} e^{Z_n} \exp \left( \frac{\lambda}{\mu^2} \right) = e^{(Z_n-3)} R_{eq} \]

\[ Z_n = - \left[ n^2 + \sum_{q=1}^{n+1} a_q L_q \right] / [n^2 - 1] \]

\[ L_{n+1} = \frac{1}{2n+1} [4nL_n - (2n-1)L_{n-1}] \]

\[ a_q(n) = \begin{cases} 
0.75 + (n-q) & \text{for } q = 1 \\
n-q & \text{for } q = 2, \ldots, n-2 \\
-0.5[n(n-1) + 0.25] + 1 & \text{for } q = n-1 \\
0.5 & \text{for } q = n \\
-0.5[(n+1)n + 0.25] & \text{for } q = n+1 
\end{cases} \]
$$R_n = \frac{e^{2n\Delta}}{8} e^{\lambda \mu^2}$$

$$\Xi_n = -n^2 + \frac{\sum_{k=1}^{n+1} q_i q_j \xi J/\xi n^2}{1}$$

**Unstable region**

**Stable region**

Diagram with curves for different values of $n$: $n=2, n=6, n=10, n=14$.
Potential flow in monolayer

\[ \nabla \cdot \vec{v} = \nabla^2 \varphi = 0 \]

\[ \varphi = -\frac{vR_c}{n} \left( \frac{r}{R_c} \right)^n \cos n\theta \quad \text{for } r \leq R_c \]

\[ \varphi = -\frac{vR_c}{n} \left( \frac{R_c}{r} \right)^n \cos n\theta \quad \text{for } r > R_c \]

Viscous drag from subphase: Drag \sim \text{velocity} \cdot \text{area}

**Note:**

1. Energy loss for circular domain shape:

\[ \frac{1}{2\pi} \left( \frac{2r_n}{dt} \right) \left( \frac{\partial}{\partial r_n^2} F_n \right) \]

2. Energy loss from viscous drag:

\[ \frac{2n}{2\pi} \left( \int_0^{R_c} r dr + \int_{R_c}^{\infty} r dr \right) \int_0^{\pi/n} d\theta \gamma (\nabla \phi)^2 = \gamma \left( \frac{dr_n}{dt} \right)^2 R_c^2 \left( \frac{1}{2n} + \frac{1}{2n} \right) \]

\[ r_n = A \exp \left[ -\frac{nF_n}{\gamma R_c^2 r_n^2} t \right] \]

\[ \lim_{t \to \infty} r_n = 0 \]

\[ \frac{dr_n}{dt} = -\frac{\partial \varphi}{\partial r_n} \]
Lipid domains in a drift-free environment exposed to an electric field

-ve polarity: attraction of DChol-rich domains $\rightarrow$ fusion
+ve polarity: repulsion of large domain formed
Mathematica version:
- amplitude: 0.17
- aspect ratio: 1.3
- rotation left: 120°
- scaled down by 70%

Mathematica version:
- amplitude: 0.085
- aspect ratio: 1.3
- rotate left: 3°
- scaled down by 57%

Mathematica version:
- amplitude: 0.07
- aspect ratio: 0.82
- rotate right: 93°
- scaled down by 63%

50μm

Figure 14
Line Tensi
Benvegnu & McConnell, JPC (92) 96, 6820

Brownian Mot.
Klingler & McConnell, JPC (93) 97, 6096

Field Gradient
Klingler & McConnell, JPC (93) 97, 2962

Field induced core grad. - exp.
Lee, Klingler, McConnell
Science (94) 263, 655

Field Induced Core grad. - Theory
Lee & McConnell
BRJ (95) 64, 1740

Shape Trans.
Lee & McConnell
JPC (93) 97, 9532
- take blood, invert bottle w/ anticoagulants
- wash & pack cells 3x using diff centrifuge speeds
dump blood in small tube (1/3)
fill 2 15mL Nacl
Spin @ 4°C 3 x 3000 rpm (5 min)
1 x 6500 rpm
Suck out yellow liquid
- Swm PBS 5 min on ice
  → lyse cell
  → remove hemoglobin
Spin hard 20 - 23k x g for 10 - 15 min
Discard supernatant
Refill & respin
- Pipette membrane out
- add 1:2 CHCl3: Mcoll
  vortex violently
- take out & pipette
  evaporate solvent under argon
  put in freezer under argon (-20°C)
- TLC plate
same critical pressure $\pi_{13}$ as the binary mixture of 2 and 3, $\pi_{31}$. Joining these binary critical points is a calculated line of critical points. Thus critical properties hold for substantial variation in lipid composition along this critical line. A lipid mixture of $n > 3$ components with interactions described by Eq. (1) has an $n - 1$ dimensional surface of critical points. In this theoretical scenario, critical behavior is sensitive to cholesterol concentration and relatively insensitive to substantial variations in phospholipid composition (cf. Table I).

Figure 3(b) gives a theoretical phase diagram for a binary mixture of components 1, 3 or 2, 3. Superimposed on this phase diagram are the structure phases $H$ and $S$. The hexagonal ($H$) and stripe ($S$) phases have length scales $D$ set by a competition between long-range intermolecular dipole repulsions and interdomain line tension $\lambda$.

$$D = (d e^\lambda)^{1/2},$$  \hspace{1cm} (3)

Here $m$ is the difference in dipole density in the two phases and $d$ is the order of a nearest neighbor intermolecular distance. Near the critical point the widths of the stripes are equal to $d e^{\lambda/2}$ [4]. The line tension $\lambda$ and the dipole energy difference term $m$ are related to the pressure difference $(\pi - _{13})$ by critical exponents $\mu = 1$ and $\beta \approx 0.25$, respectively [14,17,18]. Hence, as $\pi$ approaches $\pi_c$, $D$ decreases. $D$ is the stripe width or circular domain radius. Indeed, in a binary mixture of cholesterol and phosphatidylethanolamine, we have observed that the stripe width approaches zero as the surface

---

**Table I.** Molar lipid compositions were mixed to approximate the compositions of the inner and outer leaflets of the red blood cell membrane. Concentrations are given for cholesterol (Chol), the four other major lipid species (sphingomyelin (SM), phosphatidylethanolamine (PC), phosphatidylcholine (PE), and phosphatidylserine (PS)), glycolipids (Gly), and the fluorescent probe Texas Red-DMPPE (dimyristoylphosphatidylethanolamine). (See Ref. [15].) Experiments 1, 2, 3, and 4 displayed critical pressures, $\pi_c$ (dyn/cm or mN/m) as in Figs. 1 and 2. Of these, experiments 1 and 4 were best estimates of the inner and outer red blood cell leaflet compositions. Experiments 2 and 3 were variations on the inner leaflet 1. Experiments 5 through 10 were variations on the outer leaflet 4. These six exhibited immissible liquid phases and a transition at high pressure (>>20 dyn/cm) to a homogeneous liquid, but no fingering or stripe phase (No). Lipids extracted [16] from the red blood cell membrane but not yet separated by headgroup contained the sum of all the cholesterol and the four major lipid species of the inner and outer leaflets, with no glycolipids. Monolayers of this "total" mixture also exhibited immissible liquid phases and a transition at high pressure (>>15 dyn/cm) to a homogeneous liquid, but no critical behavior.

<table>
<thead>
<tr>
<th>Expt</th>
<th>Chol</th>
<th>SM</th>
<th>PC</th>
<th>PE</th>
<th>PS</th>
<th>Gly</th>
<th>TR</th>
<th>$\pi_c$</th>
</tr>
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<tbody>
<tr>
<td>Inner red blood cell leaflet</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>46.2</td>
<td>5.3</td>
<td>7.4</td>
<td>28.4</td>
<td>12.5</td>
<td>0</td>
<td>0.2</td>
<td>22</td>
</tr>
<tr>
<td>2</td>
<td>40.9</td>
<td>5.8</td>
<td>8.1</td>
<td>31.2</td>
<td>13.8</td>
<td>0</td>
<td>0.2</td>
<td>25</td>
</tr>
<tr>
<td>3</td>
<td>51.5</td>
<td>4.8</td>
<td>6.7</td>
<td>25.6</td>
<td>11.2</td>
<td>0</td>
<td>0.2</td>
<td>23</td>
</tr>
<tr>
<td>Outer red blood cell leaflet</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>43.4</td>
<td>22.5</td>
<td>23.4</td>
<td>6.3</td>
<td>0</td>
<td>4.2</td>
<td>0.2</td>
<td>29</td>
</tr>
<tr>
<td>5</td>
<td>45.3</td>
<td>25.7</td>
<td>26.7</td>
<td>2.1</td>
<td>0</td>
<td>0</td>
<td>0.2</td>
<td>No</td>
</tr>
<tr>
<td>6</td>
<td>40.4</td>
<td>28.0</td>
<td>29.1</td>
<td>2.3</td>
<td>0</td>
<td>0</td>
<td>0.2</td>
<td>No</td>
</tr>
<tr>
<td>7</td>
<td>36.1</td>
<td>29.9</td>
<td>31.2</td>
<td>2.6</td>
<td>0</td>
<td>0</td>
<td>0.2</td>
<td>No</td>
</tr>
<tr>
<td>8</td>
<td>32.9</td>
<td>31.9</td>
<td>33.2</td>
<td>1.8</td>
<td>0</td>
<td>0</td>
<td>0.2</td>
<td>No</td>
</tr>
<tr>
<td>9</td>
<td>25.3</td>
<td>35.2</td>
<td>36.5</td>
<td>2.8</td>
<td>0</td>
<td>0</td>
<td>0.2</td>
<td>No</td>
</tr>
<tr>
<td>10</td>
<td>82.1</td>
<td>4.6</td>
<td>4.8</td>
<td>0.4</td>
<td>0</td>
<td>7.9</td>
<td>0.2</td>
<td>No</td>
</tr>
</tbody>
</table>
FIG. 2. Epifluorescence micrographs of a lipid monolayer simulating the erythrocyte membrane outer leaflet (Table I, expt 4). The phases and isotherms are similar to Fig. 1. (a) 12.1 dyn/cm (or mN/m): circular liquid domains <10 μm. (b) 26.1 dyn/cm: coalescence of domains. (c) 28.4 dyn/cm: fingering characteristic of critical point behavior. (d) 29.1 dyn/cm: critical point. (e) 34.5 dyn/cm: homogeneous liquid. (f) 28.8 dyn/cm: immiscible liquid phases reappear as pressure decreases. The domains exhibit fingering characteristic of proximity to a critical point. At lower pressures, the domains are circular.

FIG. 3. (a) Schematic ternary phase diagram with mole fractions X1, X2, and X3, where X1 + X2 + X3 = 1. Components 1 and 2 are phospholipids and 3 is cholesterol. At pressures π < π13 = π23, two immiscible liquid phases (2φ) coexist under the surface shown. Above this surface, there is one homogeneous liquid phase (1φ). In this model, all pure components are assumed to have equal chemical potentials µi, and surface areas, with area contraction parameters α13 = α23, α12 = 0. Binary phase diagrams for 1,3 and 2,3 appear above the X1 and X2 axes. Both pairs are assumed to have equal critical pressures π13 = π23. A line of critical points connects the two binary critical points. (b) Schematic theoretical phase diagram of cholesterol-phospholipid binary mixture. Below the critical pressure and within the two phase region three superstructure morphologies are expected, two hexagonal phases (H and H') and a stripe phase (S) [31]. The boundary between the stripe phase and the hexagonal phase is adapted from [32]. Coexistence regions of adjacent phases are in grey. The equilibrium widths of the stripes and the radii of circles depend on the proximity to the critical point, as sketched. (c) Schematic experimental phase diagram of cholesterol-phospholipid binary mixture. Stripes are observed only within a few dyn/cm of the critical point [19]. At lower surface pressures, domains are primarily black circles on a white background or reversed. Fingering is observed in the grey region, at the transition between circular domains and stripes.

pressure is raised to the critical pressure. As the critical pressure is approached from below, preexisting circular domains show fingering and then transform to the stripe phase when the composition is close to the critical composition (data not shown). At low monolayer pressures λ ~ 1.8 × 10⁻⁷ dyn and m² ~ 10⁻⁸ cgeseu and D is extremely large [18]. Theoretically, at equilibrium a stripe phase should appear over a large region of the phase diagram [Fig. 3(b)]. In contrast, stripe phases are experimentally observed only within 1–2 dyn/cm of the critical point [Fig. 3(c)] [19]. This is related to the fact that the rate of domain size equilibration is slow and that stripes produced experimentally are limited in length [20].

In our experience, these conclusions apply equally well to multicomponent mixtures. Figure 3(c) illustrates the experimental relations between circular domains, fingering domains, and the stripe phase.

The erythrocyte lipid bilayer may be near a critical point since stripe phase fingering is observed in erythrocyte lipid monolayers at comparable molecular densities. We observe critical behavior at molecular areas of ~60 Å² for the simulated erythrocyte outer leaflet and ~100 Å² for the inner leaflet. (A transition from two liquid phases to one liquid phase is found at ~40 Å² for the total lipid mixture.) Uncertainties in these areas due to the chemical assay used [21] are estimated to be less than a factor of 2. The average area of a lipid in an erythrocyte membrane of a phospholipid bilayer is comparable, ~40 or ~60 Å², respectively [22,23].

Additional comparison between monolayers and the erythrocyte membrane is provided by the work of Demel et al. [24]. These investigators compared the activity of phospholipases on erythrocyte membranes to their activity on lipid monolayers at various pressures. They concluded that a monolayer pressure between 31 and 34.8 dyn/cm yields a susceptibility to this lipase activity equivalent to the susceptibility of erythrocyte membranes to lipase activity. This surface pressure is slightly higher than the pressure at which we observe critical behavior in the simulated inner and outer red blood cell leaflets.

The proximity of red blood cell lipids to a liquid-liquid immiscibility critical point should play a significant role in the cellular physical properties. For example, theoretically, membrane lipid composition and curvature
FOLDING TRANSITIONS ALSO OBSERVED IN PURE PHOSPHOLIPID SYSTEMS

DPPG
\[
\text{CH}_3(\text{CH}_2)_{14}\text{COO-CH}_2
\]
\[
\text{CH}_3(\text{CH}_2)_{14}\text{COO-CH}^-
\]
\[
\text{H}_2\text{COP(O)}_2\text{O-(CH}_2\text{)}_\cdot-(\text{CHOH})_\cdot-(\text{CH}_2\text{OH})
\]

anionic

DPPE
\[
\text{CH}_3(\text{CH}_2)_{14}\text{COO-CH}_2
\]
\[
\text{CH}_3(\text{CH}_2)_{14}\text{COO-CH}^-
\]
\[
\text{H}_2\text{COP(O)}_2\text{O-(CH}_2\text{)}_\cdot-(\text{CH}_2\text{)}_\cdot-(\text{NH}_3^+ )
\]

zwitterionic

Both have comparable head-to-tail ratio and collapse via folds in 2 mM Ca$^{2+}$, 150 mM NaCl, 0.2 mM NaHCO$_3$, pH 6.9

DPPC
\[
\text{CH}_3(\text{CH}_2)_{14}\text{COO-CH}_2
\]
\[
\text{CH}_3(\text{CH}_2)_{14}\text{COO-CH}^-
\]
\[
\text{H}_2\text{COP(O)}_2\text{O-(CH}_2\text{)}_\cdot-(\text{N(CH}_3)_3^+ )
\]

zwitterionic

DPPC has a large head compared to the tails and does not form folds under any experimental condition

Can we make DPPC form folds like DPPG and DPPE by adding another surfactant to DPPC?
What can be the cause for the folding transition?

- Both DPPG (anionic) and DPPE (zwitterionic) fold
  - electrostatics cannot be the controlling factor

- In some systems, folds are observed on pure water subphase, they do not occur when 150 mM NaCl is added, but reoccurred when small amount of divalent ions are added
  - divalent ions may act to dimerize the lipids, helping them pack tighter

- The main difference between DPPG or DPPE and DPPC is the presence of the head/tail size mismatch in DPPC
  - the ability to pack tightly may allow the film to have enough rigidity for the folding transition

To rectify the head/tail size mismatch in DPPC

- DPPC \textit{zwitterionic} + Palmitic Acid (PA) \textit{anionic} mimics

- DPPC \textit{zwitterionic} + Hexadecanol (HD) \textit{zwitterionic} mimics
Folding does occur in some of these mixed binary systems!
High Intensity

SLAC
ANL (APS)
ALS
BNL
ESRF
DESY
Bellin

\[ \lambda \approx 1.3 \text{ Å} \]

Incident angle \( \alpha_i = 0.11^\circ = 0.00185 \alpha_c \)

Total ext. reflection
evanescent wave
max surface intensity

Large footprint

5 mm x 50 mm
1 mm x 50 mm
Fig. 2 (Ka Yee C. Lee et al.)
Grating Incident Diffraction (GIXD)

3D: Bragg spots

2D: Bragg rods
   (each of vertical crystalline repeat)

\[ q_{xy} = \frac{4\pi}{\lambda} \sin \frac{2\theta_{xy}}{2} \]

Bragg peak \( \rightarrow \) \( \int \) over \( \Omega_{2\pi} \)
Bragg rod profile \( \rightarrow \) \( \int \) PSD channel

d spacing of 2D lattice
\[ d = \frac{2\pi}{q_{xy}} \]

Line shape of peak

2D coherence length \( L \)

Intensity distribution along Bragg rod direction + way of molec. tilt. out of plane coherence \( L_c \)

surface roughness
Fig. 3 (Ka Yee Lee et al.)
PA, 15mN/m, 16°C, \{1,1\}_\text{rect} and \{0,2\}_\text{rect} Bragg rods

![Graph showing intensity vs. Q_z (Å⁻¹)]

Fig. 4 (Ka Yee C. Lee et al.)
PA/SP-B1-25 ON PURE WATER @ 16 °C - GIXD DATA

**without protein**

- **16°C**
  - 30 mN/m
  - 15 mN/m

**with protein**

- **16°C**
  - 40 mN/m
  - 15 mN/m

**Observed d-spacing (Å) Area per molecule (Å^2) Unit cell axis (Å) Coherence length (Å)**

<table>
<thead>
<tr>
<th></th>
<th>d11</th>
<th>d02</th>
<th>a</th>
<th>L11</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA 15 mN/m</td>
<td>4.33</td>
<td>4.19</td>
<td>5.06</td>
<td>155</td>
</tr>
<tr>
<td>PA/SP-B (15 mN/m)</td>
<td>4.33</td>
<td>4.20</td>
<td>5.06</td>
<td>129</td>
</tr>
<tr>
<td>PA (30 mN/m)</td>
<td>4.14</td>
<td></td>
<td>4.78</td>
<td>468</td>
</tr>
<tr>
<td>PA/SP-B (40 mN/m)</td>
<td>4.13</td>
<td></td>
<td>4.77</td>
<td>451</td>
</tr>
</tbody>
</table>

- Reduction in scattering intensity in the presence of protein is due to the creation of a disordered phase in the surface film (agrees with microscopy results)
- Protein resides in the disordered phase

essentially identical for both the cases with and without protein
Fig. 10 (Ka Yee C. Lee et al.)
Electron density distribution in the direction normal to the interface.

Analysis using slab model:
- Each slab: constant electron density and thickness.
- Interface: smeared out 2 Gaussian functions.

Unit cell:
\[ \frac{1}{a_0^2} = \frac{1}{d_{y}^2} + \frac{1}{(2d_{02})^2} \]
- rectangular
\[ a_y = \frac{d}{\cos 30^\circ} \]
- hexagonal

Orthorhombic: 2 molecules/cell
- Chains in henrybone structure.

Triclinic:
- 1 molecule/cell
**PA/SP-B1-25 ON PURE WATER @ 16 °C - X-RAY REFLECTIVITY DATA**

**without protein**  
15 mN/m

- head + H₂O: 4.2Å  
- tail: 16.8Å  
- total length: 21Å  
- area/mol.: 21.8Å²  
- roughness: 2.9Å

**with protein**  
40 mN/m

- protein-water: 9.5Å  
- head-protein: 2.7Å  
- tail-protein: 5.1Å  
- tail: 11.9  
- total length: 29.2Å  
- area/mol.: 25.3Å²  
- roughness: 2.3Å

**Diagram Notes:**
- **a** and **a'** show the reflectivity curves for without protein.
- **b** and **b'** show the reflectivity curves for with protein.
- The diagrams depict the density profile of water and the molecular structure of the protein.
INSERTION OF SP-B1-25 INTO LIPID MATRIX

angle of insertion = 34° relative to the interface

Biophys. J. 81 (2001) 572-585
GIXD DATA ON PURE WATER

DPPC/PA

15 mN/m, 30°C

Intensity [counts]

1.20 1.30 1.40 1.50 1.60 1.70
Q_{xy} [Å^{-1}]

10^4 10^5 10^6

PA
1:4 DPPC:PA
1:2 DPPC:PA
1:1 DPPC:PA
3:1 DPPC:PA
DPPC

DPPC/HD

15 mN/m, 30°C

Intensity [counts]

1.20 1.30 1.40 1.50 1.60 1.70
Q_{xy} [Å^{-1}]

10^4 10^5 10^6

HD
1:2 DPPC:HD
1:1 DPPC:HD
3:1 DPPC:HD
DPPC

DPPC/PA

40 mN/m, 30°C

Intensity [counts]

1.20 1.30 1.40 1.50 1.60 1.70
Q_{xy} [Å^{-1}]

10^4 10^5 10^6

PA (30 mN/m, 30°C)
1:4 DPPC:PA
1:2 DPPC:PA
1:1 DPPC:PA
3:1 DPPC:PA
DPPC

DPPC/HD

40 mN/m, 30°C

Intensity [counts]

1.20 1.30 1.40 1.50 1.60 1.70
Q_{xy} [Å^{-1}]

10^4 10^5 10^6

HD
1:2 DPPC:HD
1:1 DPPC:HD
3:1 DPPC:HD
DPPC
<table>
<thead>
<tr>
<th>Composition</th>
<th>Observed ( d )-spacings (Å)</th>
<th>Area per chain (Å²)</th>
<th>Projected area per chain (Å²)</th>
<th>Unit cell (Å)</th>
<th>Coherence length, ( L ) (Å)</th>
<th>Tilt angle, ( \tau ) (degrees)</th>
<th>Tilt direction (degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DPPC</td>
<td>( d_{11} ) 4.57, ( d_{02} ) 4.31</td>
<td>23.27</td>
<td>21.00</td>
<td>rectangular</td>
<td>( L_{11} ) 50, ( L_{02} ) 150</td>
<td>25.5°</td>
<td>13° from NN, non-symmetry</td>
</tr>
<tr>
<td>PA 25mN/m</td>
<td>( d_{10} ) 4.20</td>
<td>20.37</td>
<td>20.28</td>
<td>hexagonal</td>
<td>( L_{10} ) 720</td>
<td>5.3°</td>
<td>NN</td>
</tr>
<tr>
<td>DPPC:PA 3:1</td>
<td>( d_{11} ) 4.35, ( d_{01} ) 4.33, ( d_{11} ) 4.25</td>
<td>21.43</td>
<td>19.97</td>
<td>oblique</td>
<td>( L_{10} ) 70, ( L_{01} ) 160, ( L_{11} ) 700</td>
<td>21.3°</td>
<td>14.9° from NN, non-symmetry</td>
</tr>
<tr>
<td>DPPC:PA 1:1</td>
<td>( d_{10} ) 4.19</td>
<td>20.28</td>
<td>20.22</td>
<td>hexagonal</td>
<td>( L_{10} ) 490</td>
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<tr>
<td>DPPC:PA 1:2</td>
<td>( d_{10} ) 4.18</td>
<td>20.19</td>
<td>20.15</td>
<td>hexagonal</td>
<td>( L_{10} ) 560</td>
<td>3.8°</td>
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<tr>
<td>DPPC:PA 1:4</td>
<td>( d_{10} ) 4.18</td>
<td>20.19</td>
<td>20.13</td>
<td>hexagonal</td>
<td>( L_{10} ) 600</td>
<td>4.5°</td>
<td>NN</td>
</tr>
</tbody>
</table>
OPTIMAL PACKING AND POSSIBLE ARRANGEMENTS IN 2D

Data

Model

A

\[ A_{\text{chain}} (\text{Å}^2) \]

\[ \Delta A/A_{\text{chain}} \]

\[ t (\text{°}) \]

\[ \chi_{\text{PA}} \]

\[ \chi_{\text{HD}} \]

DPPC/HD (3:1, m:mm)
(perfect match of head and chain cross sectional areas, but unfavorable alignment of head groups)

DPPC
(head-tail-mismatch)

DPPC/HD (1:1, m:mm)
(densest packing of chains)

J. Chem. Phys., in press

- DPPC head group
- + kovalently attached palmitic acid
- • Hexadecanol
Reversible Folded Structures coexist with the monolayer.
 Collapse is predominantly by formation of either surface bound tubular vesicles or unbound vesicles. The monolayer is not biphasic at collapse.
- T < 28°C collapse takes place primarily by large scale reversible folding.
- T = 28°C, 30°C bimodal collapse with both vesiculation and folding observed.
- T ≥ 33.5°C monolayer is monophasic and only vesiculation is observed.
1. Compress the monolayer at a low temperature up to the folding point
2. Heat the subphase and watch the changes in phase and morphology
   To verify the existence of the Fold to Vesicle Boundary and Transition
Temperature Jump Morphology

Model

- domain size $L \approx 10 \, \mu m$
- domain boundary width $\xi \approx 1 \, \text{nm}$
- elastic length $\lambda = (K/\gamma)^{1/2} \approx 1\text{–}10 \, \text{nm}$
- spontaneous radius of curvature $c_0^{-1} \approx 1\text{–}10 \, \text{nm}$.

$\implies$ We focus on the vicinity of an isolated straight boundary.

$$
G = \int_A dA \left( \frac{1}{2} K c^2 - K c_0 c \right) + \gamma \int_A d(A - A_p) + \tau \int_R d(R - y) \\
g \equiv \frac{G}{L} = \int_{-\infty}^{\infty} ds \left[ \frac{1}{2} K \dot{\theta}^2 - K c_0 \dot{\theta} + \gamma (1 - \cos \theta) \right]
$$