

# Emulsifiers from Natural Resources: The Role of Lecithin in Emulsion Formation from Molecular Dynamics

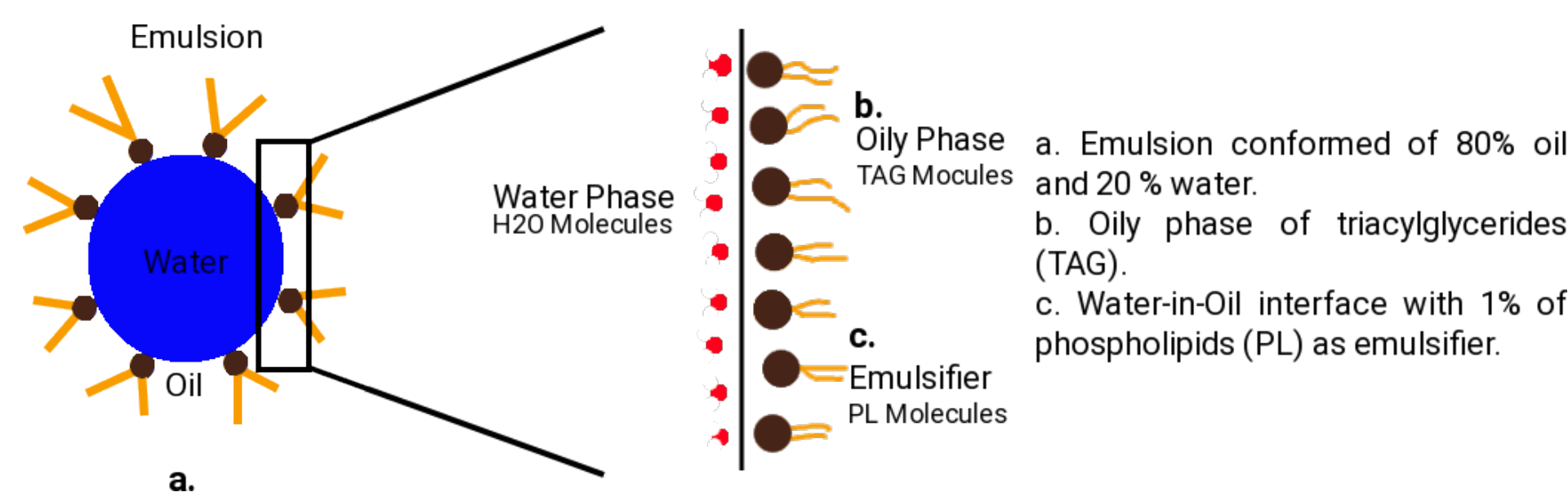
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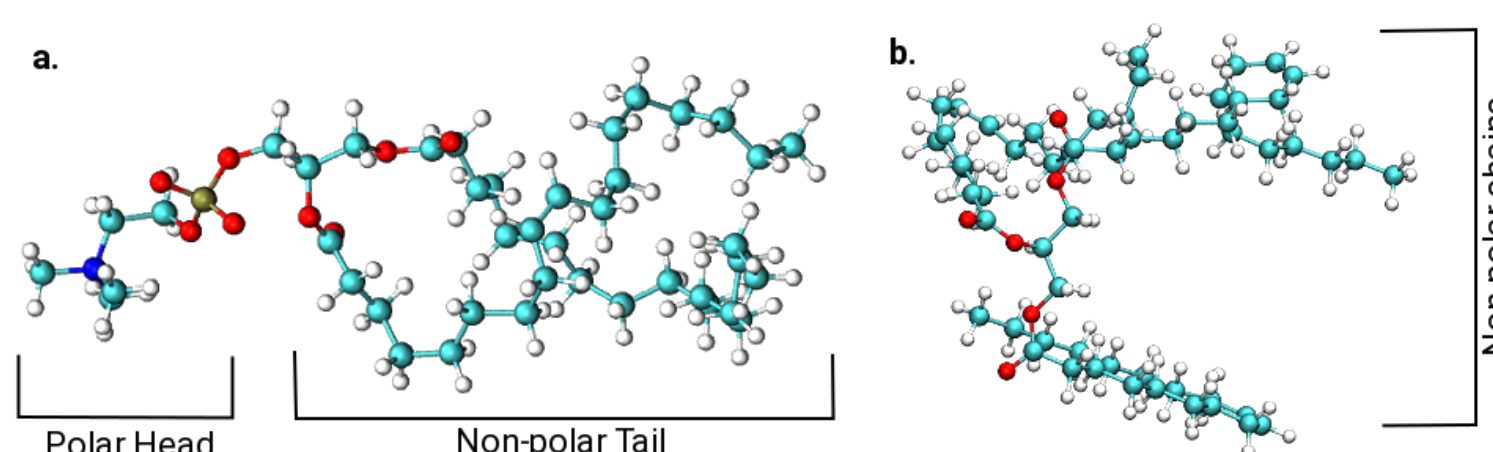
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## Motivation

Molecular Dynamics simulations can be applied to the study of physico-chemical parameters as interfacial tension of emulsions, *e. g.*, a water-in-oil interface.[1]



- Amphiphilic compounds as lecithins, are used as emulsifiers
- Lecithins are a mix of Phospholipids (PLs), Triacylglycerides (TAGs), and others compounds



## Computational Approximation

From ensembles (Eqn. 1)

$$\langle V \rangle = \iint V(p^N, r^N) \rho(p^N, r^N) dp^N dr^N \quad (1)$$

Using forcefields: Charmm 36 FF to model intramolecular interactions (Eqn. 5).

$$V(\hat{R}) = \sum_{bonds} K_b(b - b_0)^2 + \sum_{angles} K_\theta(\theta - \theta_0)^2 \quad (2)$$

$$+ \sum_{dihedrals} \sum_j K_{\varphi j}(1 + \cos(n_j \varphi - \delta_j)) \quad (3)$$

$$+ \sum_{non-bonded-pairs-ij} \varepsilon_{ij} \left[ \left( \frac{R_{min,ij}}{r_{ij}} \right)^{12} - \left( \frac{R_{min,ij}}{r_{ij}} \right)^6 \right] \quad (4)$$

$$+ \sum_{non-bonded-pairs-ij} \frac{q_i q_j}{\varepsilon_D r_{ij}} \quad (5)$$

Surface tension can be measured applying the Kirkwood-Buff expression (Eqn. 6)

$$\gamma KB = \frac{L}{2} \langle P_\perp - P_\parallel \rangle \quad (6)$$

All minimization and production runs were carried up using the INKARI High Performance Computational Scientific Cluster located at the Universidad Nacional de San Agustín (UNSA), Arequipa, Perú, which features a Silicon Graphics U-Racked Cluster with Head Node SGI 2x AMD-Opteron processors, twelve-core, 2.4 GHz, 64 GB of RAM memory DDR3 1600 MHz 4 Discs of 2TB SATA 7200 RPM, 12 Server Nodes (9x SGI), each Node server with 2 AMD Opteron twelve-core processors, 2.4GHz, 64 GB of RAM memory DDR3 1600 MHz 3 SATA 2TB Disks 7200 RPM. All simulations were set-up using the GROMACS V. 2019 Molecular Dynamics code.

## Conclusions

We successfully created a model that describes the experimental set-up. This model corresponds to a continuous oleic phase surrounded by a phospholipid phase, which is in contact with the aqueous phase of the system. Stabilization of the system shows a temperature fluctuating with a standard deviation of about 5 K... Ready to Rock

## Acknowledgments

We thank the Universidad Nacional de San Agustín UNSA - Perú and Dr. Wilson Castro for allowing us the access to INKARI and also, their collaborations in our work. We also thank the Universidad Industrial de Santander, Parque Tecnológico de Guatiguará and directors of GIFTEX - UIS, Marianny Combariza and Cristian Blanco for allowing us the acces to their labs and their constant support in our work.

## References

- [1] M. Alagumuthu, *et al.* *AIMS Mol. Sci.* 6, 1 (2019).
- [2] E. Couallier, *et al.* *J. Chem. Phys.* 148 (18), 184702 (2018).

## System Definition and Details

Based on an emulsion model with 80:20 volume proportion (80 mL TAG and 20 mL water) we calculated the number of molecules.

Compound	%Vol	Vol (mL)	Molar mass (g/mol)	# Moles	Molecules	Ratio	Total
TAG	80	80	885.000	8.28E-02	4.98E+22	1	100 <sup>a</sup>
Water	20	20	18.0150	1.11E+00	6.67E+23	13.4	1337
Compound	% Mass	Mass (g)	Molar mass (g/mol)	# Moles	Molecules	Ratio	Total
PPL	20	20	760	2.63E-02	1.58E+22	3.18E-01	34

The Volume Guesser extension from Packmol official webpage was used to estimate the volume of the system considering a volume per molecule as a proportion of its molar mass.

Compound	Molecules	Density (g / mL)	Molar Mass (g / mol)	System Volume (Å <sup>3</sup> )	Box Sides (Å)
Water	1340	0.999	18.015	40117.12	34.26
OOL	100	0.9156	885	160508.02	54.35
PPL <sup>b</sup>	34	0.917	760	44040.6	35.31

The estimated volume of each PPL, TAG and WATER interface in the Z dimension is shown. According to this proportions, Packmol software was used to construct and pack all interfaces.

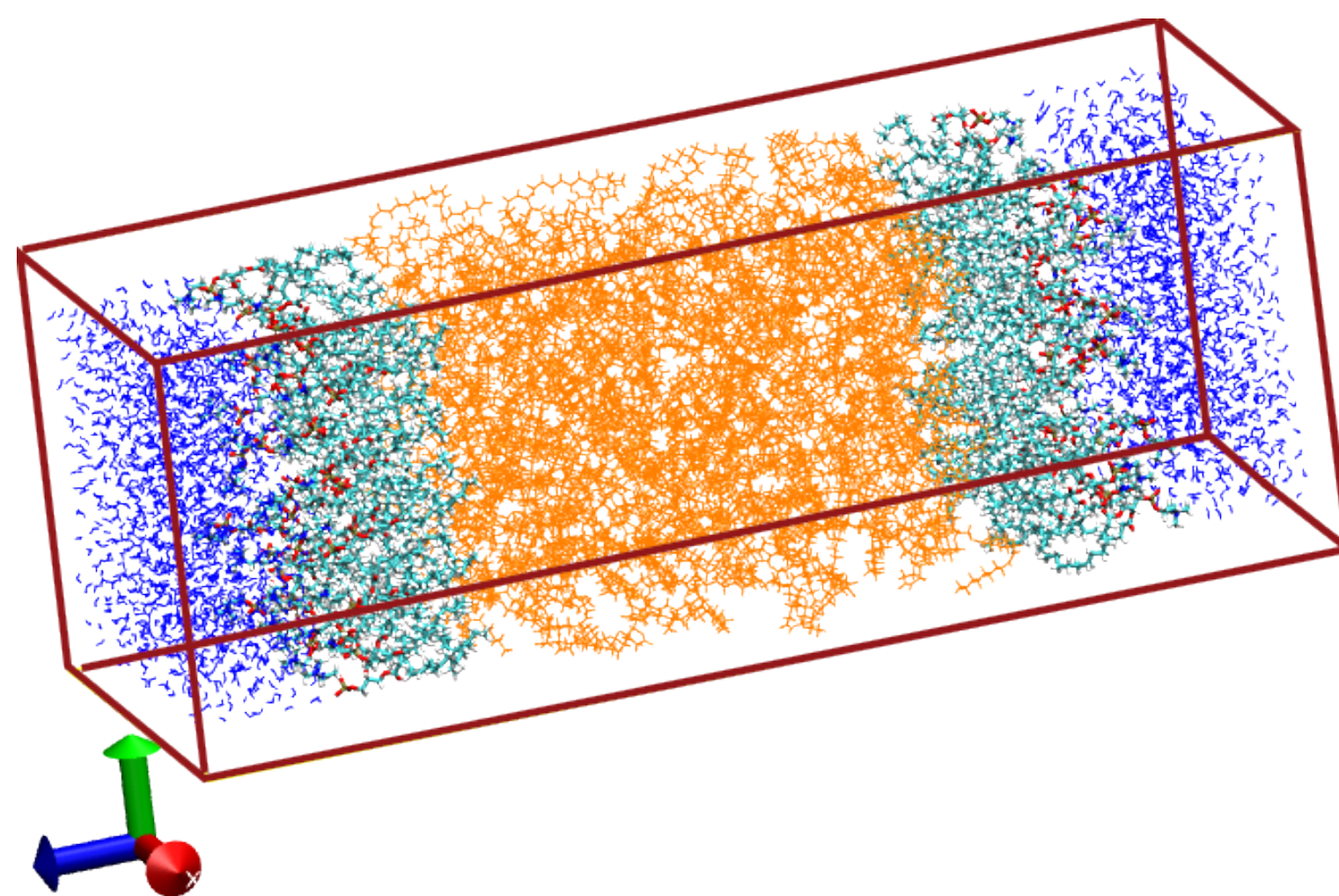
Phase/Compound	Vol. Å <sup>3</sup>	Box of side Å	Size on X	Size on Y	Size on Z.
Water	40117.12	34.26	47	47	26
OOL	160508.02	54.35	47	47	67
PPL	44040.63	35.31	47	47	28

<sup>a</sup>Density of TAG was obtained from experimental density value of sunflower oil.

<sup>b</sup>Density for PPL was obtained from experimental density of soybean oil

## Framework Simulations and Dynamics

Cell with parameters: A, B and C = 6.04350, 5.94580, 15.97680, respectively and a cubic box with alpha=beta=gamma=90, resulting in a box of 574,10 Å.



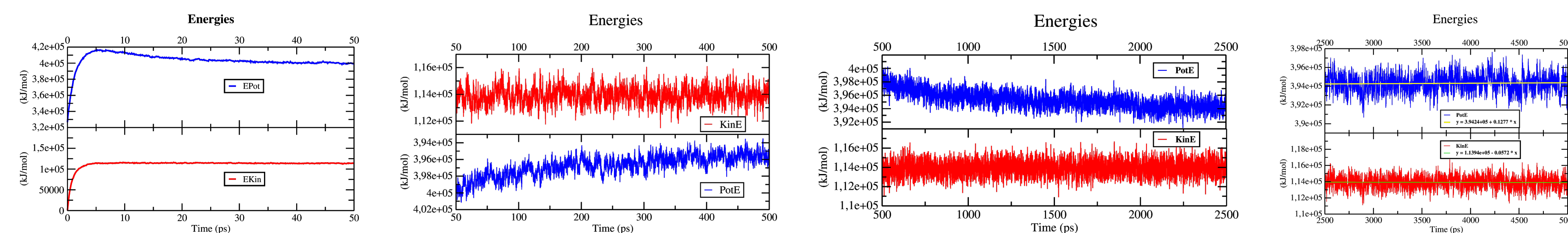
Water phase with 1337 molecules  
34 molecules of POPC with polar heads oriented towards the water  
OOL interface of 100 molecules interacting with the POPC tails  
POPC interface with 34 molecules  
Another water interface of 1337 molecules

### First step: Energy Minimization

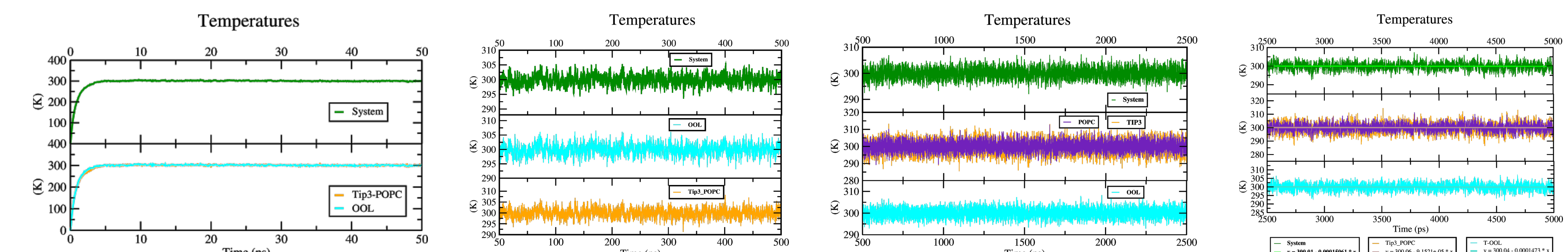
- Steepest descendent optimization for 50000 steps
- Electrostatic interactions were established by the Particle Mesh Ewald PME algorithm with a cut-off of 1.2 and a Van der Waals cut-off distance of 1.2.
- Periodic boundary conditions PBC were applied in all directions x, y, z, via the minimum image convention.

### Second step: NVT Equilibration:

- Equilibration for 550 ps, followed by an extension of 2500 ps and another one of 1000 ps
- Van der Waals radius rvdw was 1.2 as for Coulomb cut-off.
- Electrostatic interactions were set up with PME with a Fast Fourier Transform FFT of 0.16.
- Potential energy shows a drift during the first 10 ps of equilibration and a plateau for the following 40 ps.



- V-rescale thermostat was applied with an initial temperature of 300 K to two groups, that is, TIP3-POPC and OOL
- After NVT extension, thermostatic bath was set for each of the groups separately, namely, TIP3, POPC, OOL.
- Temperature shows a drift for the first 5 ps of equilibration and a tendency to stabilization at 300 K for the following 45 ps.



Production simulations are cooking right now with our beloved INKARI. But, very soon we will obtain parameters such as interfacial tension, density and interfacial thickness which will be used to contrast with experimental results obtained from physical emulsion models prepared in the lab.