Linear and Non-Linear Interfacial Dilatational Rheology of Oligo(ethylene glycol)-Based Microgels at the Air–Water Interface.

Iván Navarro-Arrebola [abc], Carmen Cara-Galdeano [a], Garbiñe Aguirre [d], Jesús Quirosa-Mancilla [a], Juan Antonio Holgado-Terriza [e], Miguel Ángel Cabrerizo-Vílchez [a], Alberto Martín-Molina [af], Julia Maldonado-Valderrama [ac].

[a] Department of Applied Physics, University of Granada (UGR), 18071 Granada, Spain, [b] Department of Applied Mathematics, UGR, [c] Modelling Nature Scientific Research Unit, UGR, [d] Bio-Inspired Materials Group: functionalities & Self-Assembly, Institute of Analytical Sciences and Physico-Chemistry for Environment and Materials (IPREM), Université de Pau et Pays de l'Adour (UPPA), 64000 Pau, France, [e] Department of Computer Science and Systems, UGR, [f] Carlos I Institute of Theoretical and Computational Physics, UGR

inarrebola@ugr.es

The interfacial mechanics of oligo(ethylene glycol) (OEG)-based microgels[1] adsorbed at the air–water interface were characterised by pendant drop tensiometry, combining linear and non-linear oscillatory dilatational protocols to resolve their viscoelastic response below and above the volume phase transition temperature (VPTT). Adsorbed layers were equilibrated at a constant surface area prior to imposing oscillatory area perturbations. In the linear regime, small-amplitude oscillations ($\Delta A/A_0$ = 5%) were applied across a frequency range of 0.01–0.2 Hz, with harmonic analysis confirming the linearity of the response.
Beyond this regime, large-amplitude oscillatory dilatation (LAOD) was employed to probe the non-linear mechanical response of the microgel-laden interfaces. Amplitude sweeps with stepwise increasing deformations ($\Delta A/A_0$ = 5, 10, 20, 30%) were performed at a fixed frequency (0.02 Hz). The complete set of harmonic contributions was analysed via general stress decomposition (GSD)[2] to separate the intracycle stress into contributions arising from genuine interfacial network interactions and those stemming from surface density changes upon compression/expansion. This distinction is unique to dilatational deformation—as opposed to shear—since surface mass is not conserved during area oscillations. This framework, combining linear and non-linear harmonic analysis, provides a systematic basis for resolving differences in interfacial film strength, structuration, and deformation tolerance between the OEG-based microgel systems.

Keywords:
Pendant Drop Tensiometry, Oligo(ethylene glycol)-based Microgels, Interfacial Dilatational Rheology, Large-amplitude oscillatory dilatation (LAOD).

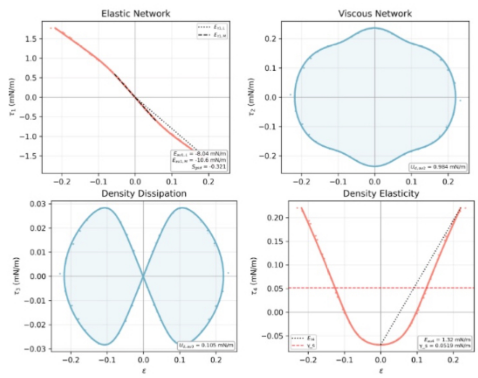

Figure: Representative GSD analysis under LAOD at the air–water interface. Total stress is decoupled into elastic and viscous network interactions (top), alongside density dissipation and density elasticity (bottom) arising from surface mass non-conservation.

References:

[1] Aguirre, G., Quirosa-Mancilla, J., Cara-Galdeano, C., Navarro-Arrebola, I., Rubio-Andres, A., Fernandez-Rodriguez, M. A., Billon, L., Martín-Molina, A. & Maldonado-Valderrama, J.; Journal of Colloid and Interface Science, 705 (2026) 139522.
[2] Risse, K., Yang, J., de Groot, A., Giménez-Ribes, G., Shen, P., Drusch, S., Hinderink, E. B.A. & Sagis, L. M.C; Advances in Colloid and Interface Science, 345 (2025) 103625.

Acknowledgements:
Supported by the "Modeling Nature" project QUAL21-11 (Junta de Andalucía); proyects C-EXP-187-UGR23 (Junta de Andalucía/ERDF 2021-2027) and PID2023-149387OB-I00 (MICIU/AEI/10.13039/501100011033 and ERDF "A way of making Europe").