Quantifying Phase Separation and Local Transport in Thermoresponsive PNIPAm Solutions Using Multiple Particle Tracking Microrheology (MPT)

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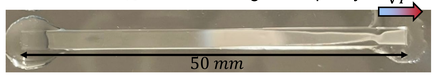
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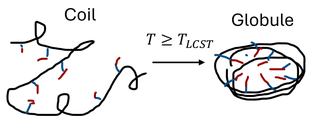
Abstract

Thermoresponsive polymers such as poly(N-isopropylacrylamide) (PNIPAm) have potential for temperature-controlled particle separation techniques. Above its lower critical solution temperature (LCST) of ~34°C, PNIPAm shrinks, expels water, and forms polymer-rich domains that restrict particle motion. While bulk PNIPAm phase behavior is well characterized, local rheology during phase separation is poorly understood. We apply a one-dimensional thermal gradient to PNIPAm solutions and use 2D multiple particle tracking microrheology to characterize particle motion across the resulting phase-separated interface. In a thermal gradient, particle displacements show distinct slow and fast populations corresponding to polymer-rich and solvent-rich regions, respectively. Across PNIPAm concentrations, the spatial distribution of populations, apparent viscosity, local heterogeneity, and particle velocity remain consistent, indicating reproducible microscale properties across the phase-separated interface. In microgravity conditions, we measure rapid particle localization at the hot side. In ground conditions, buoyancy-driven recirculation drives continuous flow toward the interface. These results characterize particle transport in thermoresponsive systems and inform design of thermal-gradient-driven separation using thermoresponsive materials as a tunable component.

Thermoresponsive Polymers for Optimized Particle Separation

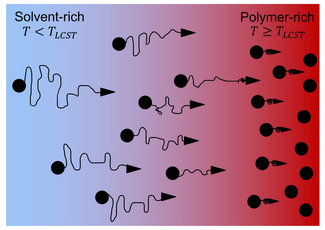
$10\ wt\%$ PNIPAm in a glass capillary





At $T \geq T_{LCST}$, PNIPAm coils undergo a phase transition and expels water

Particle trapping in a thermal gradient

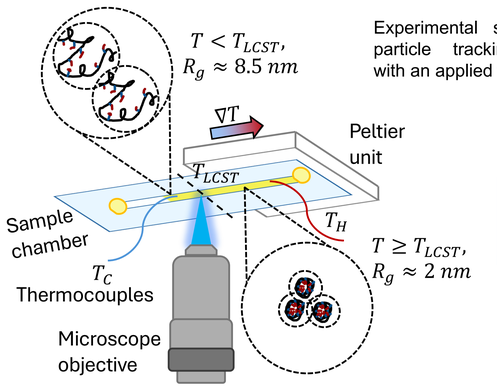


Characterizing particle transport and local rheology in a thermal gradient informs the design of thermal-gradient driven particle separation methods. In this work, we vary:

- Temperature: ∇T vs. uniform T
- PNIPAm concentration: C/C^*, where overlap concentration $C^* = 2.5\ wt\%$
- Gravity: ground vs. microgravity conditions

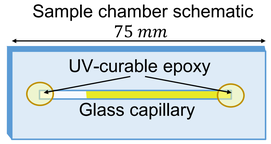
Bischofberger & Trappe, *Sci. Rep.*, 2015, 5(1), 15520

2D Fluorescence Microscopy in a 1D Thermal Gradient



Experimental setup for multiple particle tracking microrheology with an applied thermal gradient

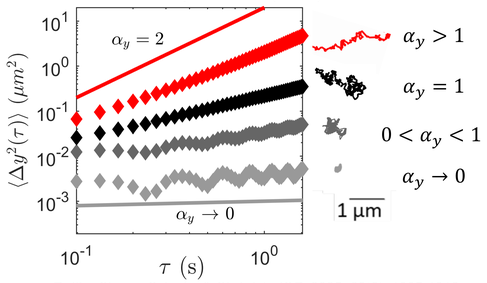
Sample chamber schematic



In a 1D thermal gradient:

- x-direction: transport velocity
- y-direction: local rheology

Ensemble-averaged mean-squared displacement (MSD) in 1D



$$\langle \Delta y^2(\tau) \rangle = 2dD_y\tau^{\alpha_y}$$

$$\alpha_{NG,y} = \frac{\langle \Delta y^4(\tau) \rangle}{3\langle \Delta y^2(\tau) \rangle^2} - 1$$

$$\eta_{app} = \frac{k_B T}{6\pi D_y a}$$

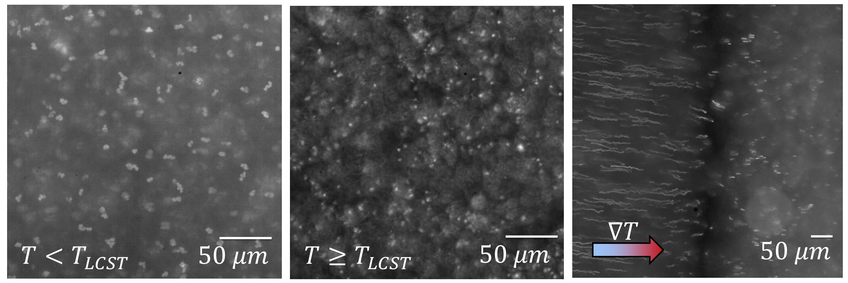
$$u_x = \left\langle \frac{1}{n} \cdot \sum_{i=1}^{n} \frac{\Delta x_i}{\Delta t} \right\rangle$$

Hasanova, Roffin, Cheng, Schultz, & Gilchrist, *JOR*, 2025, 69(6), 1005-1016.
Crocker & Grier, *J. Colloid Interface Sci.*, 1996, 179, 298–310.

Furst and Squires, *Microrheology*, 2017.

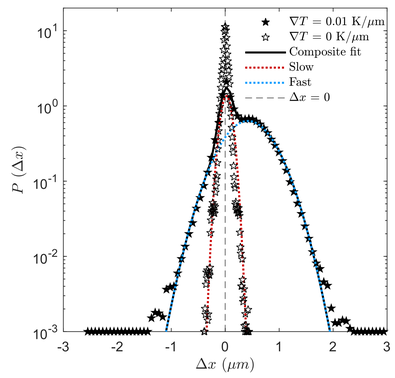
Tracking Motion of Fluorescent Particles with MPT

Temporal projections of fluorescent particle motion in $10\ wt\%$ PNIPAm



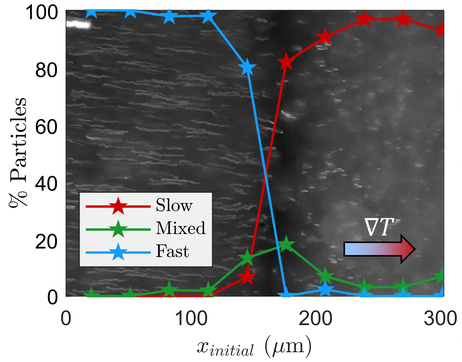
Probability distribution function of particle displacements in $10\ wt\%$ PNIPAm

$$P(\Delta x, \tau) = \frac{1}{\sqrt{4\pi D_x \tau}} \exp\left(-\frac{\Delta x^2}{4D_x\tau}\right)$$



Spatially mapped particle population profiles in $10\ wt\%$ PNIPAm

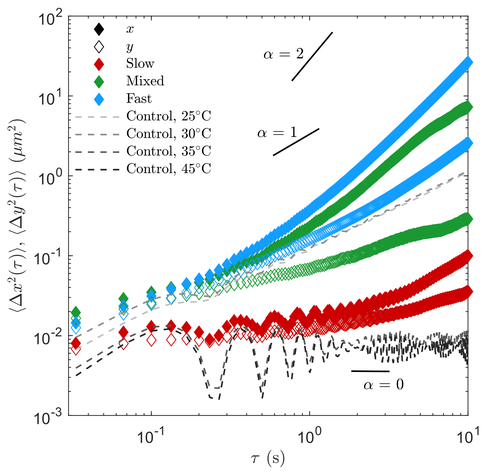
$$P(\Delta x, \tau) = f_{fast}P_{fast}(\Delta x, \tau) + f_{slow}P_{slow}(\Delta x, \tau)$$



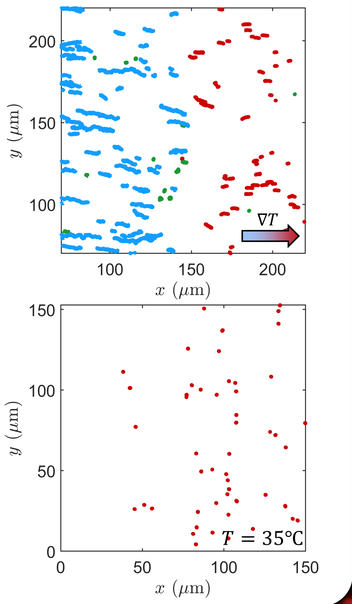
Hsiao, Kang, Ahn, Solomon, *Soft Matter*, 2014, 10, 9254.

Distinct Particle Populations Form in a Thermal Gradient

1D MSDs in the x- and y-directions, $\langle \Delta x^2(\tau) \rangle$ and $\langle \Delta y^2(\tau) \rangle$, for particle populations in $10\ wt\%$ PNIPAm at $\nabla T = 0.01\ K/\mu m$

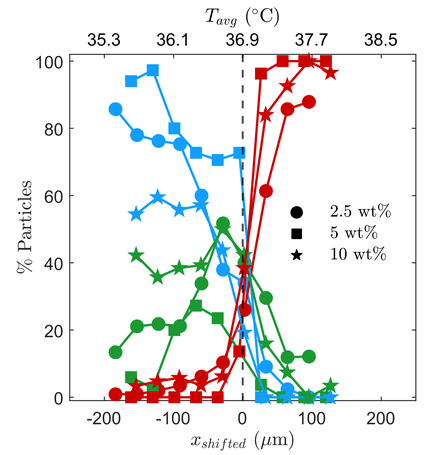


Color-coded particle trajectory maps in $10\ wt\%$ PNIPAm



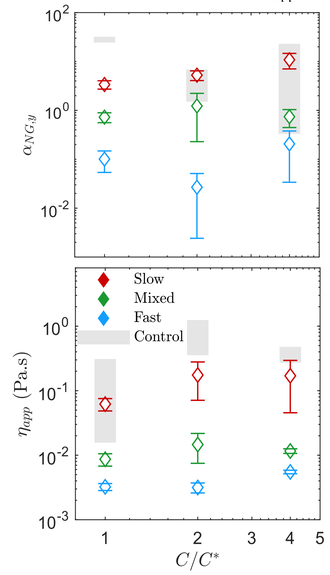
Rheology of the Interfacial Region is Reproducible Across PNIPAm Concentrations

Particle population profiles and measurement temperature, T_{avg}



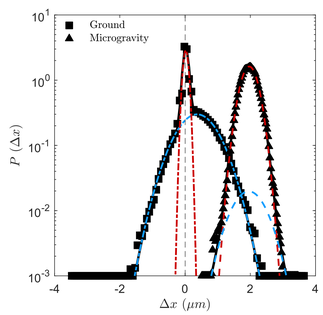
T_{avg} is estimated from experimental temperature measurements mapped to the corresponding measurement location

Non-Gaussian parameter, $\alpha_{NG,y}$, and apparent viscosity, η_{app}

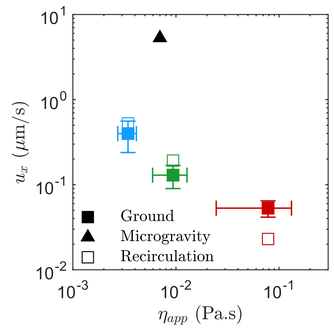


Particles Rapidly Localize in Microgravity Conditions

Probability distribution function of particle displacements in $5\ wt\%$ PNIPAm



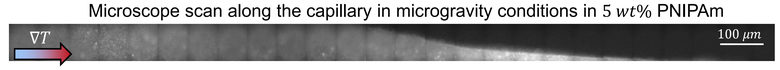
Particle velocity u_x in $5\ wt\%$ PNIPAm



Recirculation always occurs in a thermal gradient under gravity with a characteristic velocity:

$$u_r = \frac{\rho g \beta \Delta T H^3}{6\eta L}$$

Microscope scan along the capillary in microgravity conditions in $5\ wt\%$ PNIPAm



Bergé, P., & Dubois, M., *Contemp. Phys.*, 1984, 25(6), 535-582.

Future Directions

The reproducible interfacial properties of PNIPAm show promise for incorporating it as a controllable component of more complex systems for particle separation. Extending this approach to different particle types and biological fluids may enable tunable thermal-gradient driven particle focusing and separation techniques.

Acknowledgements

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