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Transport, Dynamics, and Phase Behavior of Soft Matter Under Nanoconfinement

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Abstract: Nanoscale confinement strongly alters the behavior of soft matter, from polymer crystallization to lipid self-assembly. In this mini review, we summarize recent progress on how confinement impacts molecular transport, crystallization, dynamics, and phase behavior in two distinct media: hard confinement in inorganic nanopores and soft confinement in lipidic mesophases. In the first part, we highlight polymer transport and dynamics in rigid nanopores, emphasizing how chain topology (linear, star-shaped, hyperbranched) governs confined crystallization and relaxation dynamics. In the second part, we turn to lipidic mesophases as biomimetic soft confining media, where phase transitions and molecular transport are intricately coupled to hydration and interfacial interactions. Together, these studies reveal that confinement effects arise not only from geometry but also from surface interactions, and that their interplay determines the structure and dynamics of confined matter. Understanding these principles opens avenues for applications in drug delivery, cryo-enzymology, and nanofabrication of functional materials and devices.

Keywords: Hydrodynamics · Lipidic mesophase· Nanoconfinement · Polymers

Dr. Yang Yao has been an Assistant Professor and group leader in the Department of Chemistry at the University of Basel, Switzerland, since January 2024. She obtained her PhD in 2018 from the Max Planck Institute for Polymer Research under the supervision of Prof. Hans-Jürgen Butt and Prof. George Floudas. Her doctoral dissertation, '*Imbibition, Crystallization, and Dynamics of Polymers and Water under Nanometer Confinement*', focused on the behavior of soft matter under nanoscale confinement. Following her PhD, Yang joined ETH Zürich as a postdoctoral researcher in the group of Prof. Raffaele Mezzenga. She was awarded the ETH Career Seed Award in 2021 and promoted to Senior Scientist in early 2022. Later that year, she received an ERC Starting Grant, funded by Swiss Secretariat for Education, Research, and Innovation (SERI), to investigate the physical state of water in biological systems.

1. Introduction

Soft matter, including polymers, lipids, liquid crystals, and water exhibit structures and dynamics that are highly sensitive to the environment. When these systems are confined at the nanometer scale, their behavior often deviates from the bulk, giving rise to new physical states, altered transport properties, and unexpected phase transitions.[1–4] Understanding the effects of confinement is not merely fundamental curiosity, it also supports phenomena as diverse as water retention in clays, oil recovery from porous rocks, cryoprotection in biological tissues, and the design of nanostructured materials and devices.[5–9]

Two distinct types of confinement dominate current research. Hard confinement, typically imposed by rigid inorganic nanopores such as anodic aluminum oxide (AAO) (Fig. 1a),[10–12] provides well-defined geometries that enable precise studies of transport, crystallization, and molecular dynamics of polymers. For instance, the interplay between capillary forces, chain entanglements, and entropy loss leads to imbibition behavior which deviates from the classical predictions of the Lucas-Washburn model,[12–15] while nucleation and crystallization are governed by both the pore size and chain topology.[16–18] In contrast, soft confinement, in the form of self-assembled lipidic mesophases (LMPs) (Fig. 1b),[19,20] offers a biomimetic environment closer to living systems. These lyotropic liquid crystals form rich phase polymorphs with interconnected water channels, enabling systematic control of transport and molecular encapsulation.[21] Our recent studies revealed that LMPs can stabilize the liquid state of water down to cryogenic temperatures, permitting enzymatic activity far below the bulk freezing point.[22,23] Such findings highlight how confinement can be used to expand the operational window of biomolecules and inspire new routes in cryo-enzymology, drug delivery, and nanotechnology.

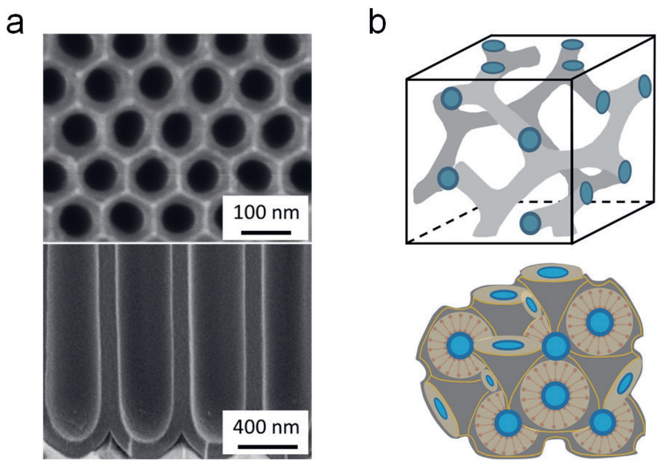

Fig. 1. a) Scanning electron microscopy images of self-ordered AAOs: (top) top view of AAO with a pore diameter of 65 nm. (bottom) cross section of AAO with a diameter of 400 nm; b) schematics of lipidic mesophase (top) gyroid $Ia\bar{3}d$ phase. (bottom) diamond $Pn\bar{3}m$ phase.

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In this mini review, we discuss recent progress on how nanoscale confinement governs soft matter behavior. We will cover the following three themes: (i) transport of polymer melts under hard confinement; (ii) crystallization and dynamics of polymers with varied topologies in nanopores; and (iii) phase behavior of lipidic mesophases under soft confinement. These examples illustrate how geometric restrictions and interfacial interactions affect the structure, dynamics, and functionality of matter at the nanoscale.

2. Transport of Polymer Melts Under Hard Nanoconfinement

How polymers penetrate into nanosized pores is a fundamental process with implications across engineering and biotechnology. Applications ranging from lab-on-chip devices and nanofluidics to membrane-based separations and nanostructured materials rely on the ability of fluids to transport in confined geometries. Filling nanoporous templates with polymers enables the fabrication of one-, two-, and three-dimensional nanostructures with tailored physical properties. Ordered AAO membranes are often employed as model hard confining systems, as they consist of parallel, cylindrical pores with tunable diameters and lengths that provide a well-defined geometry for studying polymer infiltration and dynamics.

For simple Newtonian liquids, capillary rise is well described by the classical Lucas-Washburn equation (LWE),[13] which predicts a square-root-of-time dependence of the penetration depth based on a balance between capillary driving forces and viscosity (Eqn. 1).

$$h(t) = \left(\frac{\gamma R \cos\theta}{2\eta_0}\right)^{1/2} \sqrt{t} \qquad (1)$$

Numerous studies have confirmed that the LWE model applies to macroscopic systems, with modifications to account for contact angle and surface tension. However, when the pore size approaches molecular length scales, deviations are expected. This is especially true for polymers, where chain entanglements and conformational entropy strongly influence their transport.

Unlike small molecules, polymer imbibition involves additional complexities. When the coil size of the polymer ($2R_g$) becomes comparable to or even larger than the pore diameter (Fig. 2), confinement reduces the entropy of the chains and alters their effective viscosity. Despite the entropic penalty, capillary forces typically drive polymer melts into nanopores, but the dynamics can deviate substantially from LWE predictions. Experiments have shown both faster and slower infiltration than expected, depending on the molecular weight, degree of entanglement, and pore diameter.[14] In our theoretical study, we showed that the enhanced mobility under confinement arises from a competition between two distinct mechanisms. (i) In the case of standard hydrodynamic flow, the velocity profile is parabolic. When polymer chains are attracted to the pore walls, an adsorbed layer of immobile chains forms, which slows down imbibition and increases the effective viscosity. (ii) By contrast, in the reptation model, chain motion is dominated by snake-like diffusion along the contours, leading to a plug-like flow profile.[15] This reduces the effective viscosity and accelerates imbibition. The complex transport behavior of polymer melts in nanopores can therefore be understood as the outcome of the interplay between these two opposing mechanisms.

Recent work has broadened the scope of confined polymer imbibition by examining the role of molecular weight, polydispersity, and polymer blends. For instance, differences in imbibition dynamics between short and long chains can lead to selective enrichment of pores by certain chain lengths, suggesting possible applications in polymer separation and purification.[24]

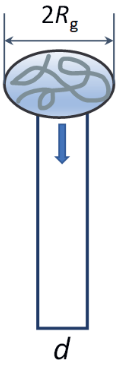

Fig. 2. Schematics of polymer imbibition when the coil size of the polymer, $2R_g$, is larger than the pore diameter d.

Confinement has also revealed unexpected transport in semicrystalline polymers: even below the melting temperature, strong capillary forces can drive flow with a viscosity intermediate between melt and crystalline states, while preserving crystalline domains.[25] Polymer imbibition into nanopores emerges as a rich, non-trivial process that goes well beyond the simple predictions of classical capillary flow models, opening opportunities for both fundamental insights and technological applications.

3. Effect of Chain Topology on Polymer Crystallization and Dynamics Under Hard Nanoconfinement

Based on the understanding of polymer melt transport under confinement, we next focus on polymer crystallization and dynamics under hard confinement, with particular attention to the effect of chain topology, linear, star-shaped, and hyperbranched, on these physical behaviors. In bulk, polymer topology strongly influences chain packing, dynamics, and crystallinity: short-chain branching reduces crystallinity, while nonlinear architectures such as stars or rings alter relaxation pathways through arm retraction or compact conformations.[26] (Fig. 3.) When confined, these effects are amplified because nucleation, orientation, and dynamics are restricted by nanoscale geometry.

For linear polymers, confinement in AAO pores typically suppresses heterogeneous nucleation, shifting crystallization towards homogeneous pathways since the diameter of the confined space is too small for impurity-driven nuclei to dominate. Crystals often adopt orientations relative to the pore axis, and segmental mobility is enhanced, as seen in reductions of the glass transition temperature (T_g). Star polymers can infiltrate nanopores despite architectural complexity. Under confinement, nucleation temperatures scale not with the total molecular weight but with the arm molecular weight, reflecting the importance of arm retraction dynamics in crystallization.[17] Their segmental relaxation is also accelerated compared to the bulk, suggesting that confinement partially releases topological constraints. Hyperbranched poly(ethylene oxides) (*hb*PEOs) represent an extreme case of nonlinear topology. Branching frustrates crystallization in the bulk, lowering crystallinity and broadening transitions. In confinement, the imbibition of *hb*PEOs in nanopores is slower than predicted by classical models but they still crystallize predominantly *via* homogeneous nucleation. Again, nucleation temperatures scale with the effective weight of the linear segments between branching points, underscoring the role of long-range chain mobility. T_g is also reduced under confinement, consistent with accelerated dynamics.[18]

In general, confinement shifts polymer crystallization from impurity-controlled heterogeneous nucleation processes toward a homogeneous mechanism governed by molecular architecture and dynamics. Across different topologies, three general trends emerge: (i) suppression of heterogeneous nucleation in favor

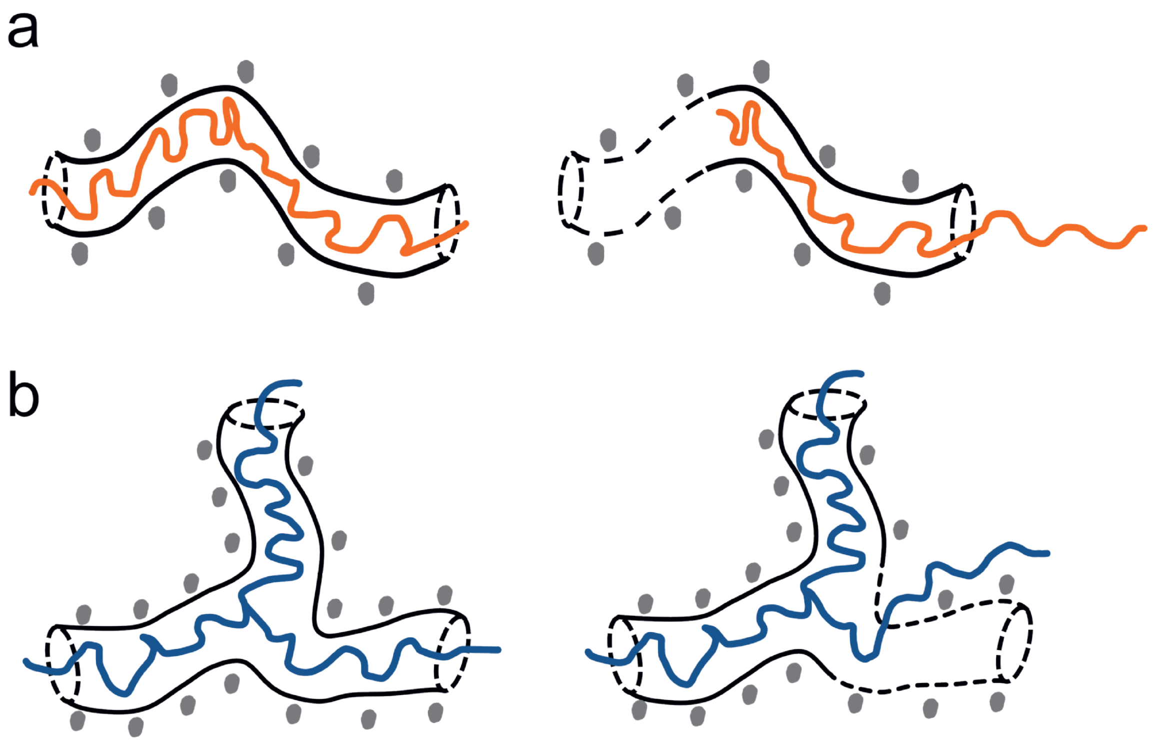

Fig. 3. Schematic of (a) reptation model for a linear polymer chain; and (b) a star-shaped polymer in the network of obstacles. The diagram is based on a Fig. from ref. [26].

of homogeneous nucleation; (ii) dependence of nucleation temperature on the effective molecular weight of mobile chain segments; and (iii) accelerated segmental dynamics with reduced T_g. These findings demonstrate the central role of chain topology in confined crystallization and point towards new strategies for tailoring polymeric nanostructures with controlled crystallinity and dynamics.

4. Phase Behavior of Lipidic Mesophases Under Soft Confinement

Contrary to the rigid confinement imposed by AAO nanopores, LMPs provide a biomimetic form of soft confinement, highly relevant for both biological and technological applications. These lyotropic liquid crystals arise from the self-assembly of amphiphilic lipids with water, giving rise to diverse phase structures, including lamellar (L_α), bicontinuous cubic (gyroid, $Ia\bar{3}d$, diamond, $Pn\bar{3}m$, primitive, $Im\bar{3}m$), reverse hexagonal (H_{II}), and micellar (L_2) phases.[19,20] In these structures, water is confined within nanoscopic domains defined by the lipid matrix. LMPs act as versatile hosts for the transport, storage, and release of guest molecules, with bicontinuous cubic and related phases offering interconnected aqueous channel networks that mimic biological environments.[21,27,28] Their three-dimensional periodicity, biocompatibility, and structural tunability enable systematic control over diffusion, governed jointly by mesophase geometry and the physicochemical properties of the lipid. Notably, all these applications depend on a fundamental understanding of both phase structure and interfacial interactions, which together decides the function of confined systems.

Our research has focused on phase transitions in lipidic mesophases and their associated molecular interactions. In phytantriol-based systems, we demonstrated that lipidic mesophases can stabilize unconventional states of water. Small angle X-ray scattering (SAXS) (Fig. 4a) is an important scattering technique to determine the phase structure and water channel diameter. Phase diagrams revealed that bicontinuous cubic phases remain stable down to –10 °C, while lamellar phases preserve liquid water to as low as –120 °C.[22,23,29] Remarkably, such conditions enabled enzymatic reactions in nanoconfined water at cryogenic temperatures, opening new opportunities in cryo-enzymology.

Spectroscopic investigations further elucidated the role of confined water. Using broadband dielectric and infrared spectroscopy (Fig. 4b), we identified two dynamically distinct fractions: bound water at lipid headgroups and interstitial free water. Both populations relax more slowly than bulk water, with the bound fraction slowed by up to three orders of magnitude. During the cubic-to-hexagonal transition, the proportion of bound water increases, consistent with the enlarged interfacial area of the H_{II} phase.[30] The presence of excess water introduces additional effects: once saturation is reached, excess water remains external but can still penetrate lipid headgroups, forming new hydrogen bonds with carbonyl groups.[31]

We also probed the dynamics of the lipid matrix itself. Broadband dielectric spectroscopy showed that confined water plasticizes lipid dynamics, accelerating its relaxation processes. In anisotropic phases, such as $Ia\bar{3}d$ and L_α, additional dipole-matrix interactions emerge. Notably, similar behavior was observed when water was replaced with glycerol, highlighting the generality of phase structure determined dynamics across different solvents.[32]

5. Conclusion and Outlook

In this review, we have discussed how nanoconfinement governs the transport, dynamics, and phase behavior of soft matter. In hard confinements such as AAO nanopores, polymer imbibition deviates from the classical Lucas-Washburn model due to the interplay of hydrodynamic flow, surface-induced chain adsorption, and reptation dynamics. These effects transform viscosity, mobility, and even morphology, giving rise to unexpected nanostructures. Confinement also reshapes crystallization pathways: in smaller pores, heterogeneous nucleation is suppressed in favor of homogeneous nucleation, governed by chain topology and long-range dynamics. Across linear, star, and hyperbranched polymers, nucleation temperatures scale consistently with the

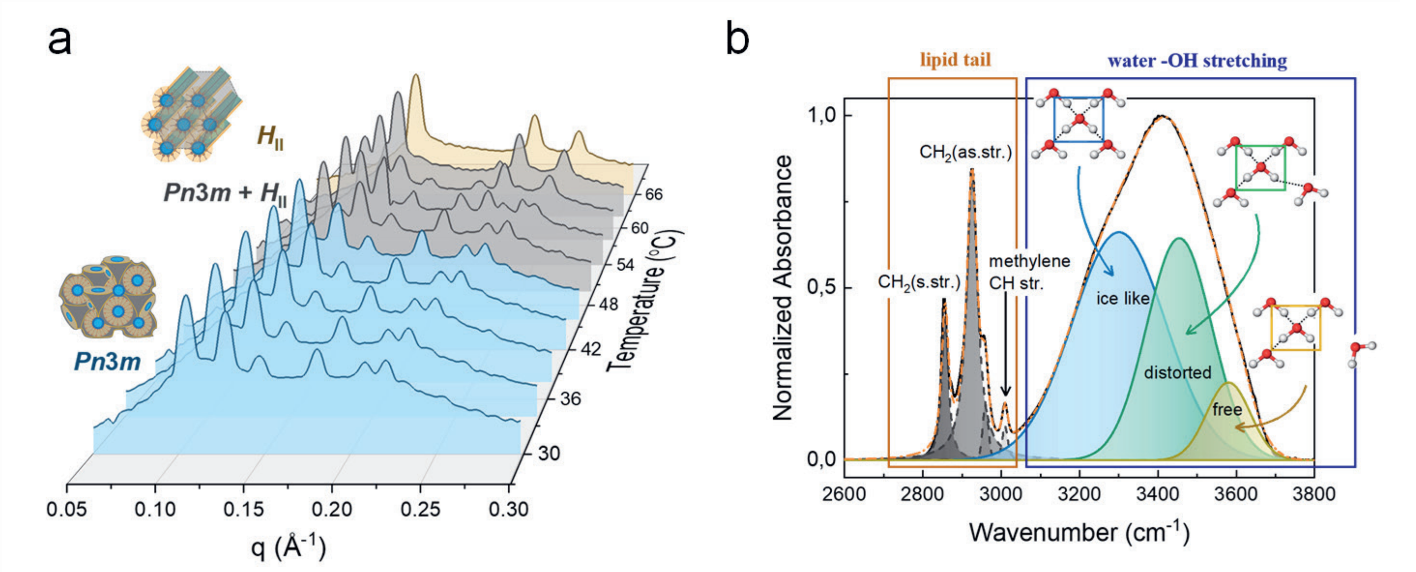

Fig. 4. a) SAXS profile of dimodan70-water30 in weight mesophase as a function of temperature; b) Example of a FTIR spectrum (region 2700–3800 cm^{-1}) of the dimodan70-water30 sample at 30 °C. The insert small schematics represent the three types of OH stretching in the water network. Figs. are adapted from ref [31], under a Creative Commons CC BY license.

effective molecular weight of the mobile chain segments, rather than the total molecular weight. Furthermore, confinement accelerates segmental dynamics and lowers glass transition temperatures, underscoring its profound influence on polymer relaxation.

In contrast, lipidic mesophases provide a biomimetic form of soft confinement, where lipids and water self-assemble into ordered geometries with interconnected channels. These mesophases stabilize unconventional states of water, maintaining liquid well below the bulk freezing point and enabling enzymatic activity under cryogenic conditions. Confined water not only governs hydration but also plasticizes lipid matrices, accelerating relaxation. In anisotropic phases, additional dipole–matrix interactions emerge, observed in both water- and glycerol-based systems.

Taken together, studies of polymers in AAO and lipids in mesophases illustrate that confinement effects stem from the interplay between geometric restrictions and interfacial interactions. The balance of these factors dictates the emergent structure and dynamics of confined matter. Looking ahead, confinement offers exciting opportunities: in polymers, for designing nanostructures with programmable crystallinity, selective chain separation, and enhanced properties; in lipids, for developing cryo-enzymatic platforms, responsive drug delivery carriers, and bio-inspired nanodevices. Combining hard and soft confinements may even enable hybrid systems that integrate the precision of inorganic templates with the adaptability of lipidic assemblies.

Therefore, confinement should not be regarded as a constraint but embraced as a powerful design principle for controlling function in soft matter, with impacts ranging from fundamental physics to applications in biotechnology, nanomedicine, and advanced materials.

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Author Contributions

Y. Yao designed the structure of the review and drafted the manuscript.

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