Learning Nonlinear Dissolution Trajectories in Binary Polymer–Solvent Systems

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1. Introduction

Binary solvent mixtures are widely used to tune dissolution behaviour in polymer systems, yet their effects remain difficult to rationalise. Unlike single-solvent dissolution, which often varies monotonically with solvent quality, binary mixtures frequently exhibit strongly nonlinear responses to composition and temperature. Commonly observed behaviours include asymmetric dissolution, cooperative cosolvency [1], competitive cononsolvency [2], and re-entrant transitions [3] between partially solvated states. These effects appear across diverse polymer and solvent chemistries, but resist description within additive or equilibrium-based models.

A central challenge lies in how polymer dissolution behaviour is represented. Classical [4] and empirical compatibility [5] descriptors assume linear mixing and collapse complex behaviour into static scalar measures, while mean-field thermodynamic models emphasise equilibrium endpoints. In practical, dissolution proceeds through a sequence of experimentally observable intermediate states, such as plasticised, swollen, dispersed, or gel-like morphologies, which encode essential information about dissolution dynamics. However, both traditional models and many recent data-driven approaches continue to frame dissolution as an endpoint classification or regression problem, discarding information about state transitions. As a result, asymmetric, cooperative, and competitive mixed-solvent effects are obscured or treated as anomalies, rather than as intrinsic features of the dissolution process.

Here, we reformulate mixed-solvent dissolution as a problem of representation learning. We introduce a continuous solvation coordinate $s \in (0,1)$, which parametrises the progression of dissolution from undissolved $(s \to 0)$ to fully dissolved $(s \to 1)$ states, while preserving the experimentally observed ordering of intermediate morphologies. Within this formulation, binary solvent systems are described by continuous trajectories $s = f(\text{polymer}, \text{solvent}_1, \text{solvent}_2, x)$, where $x \in [0,1]$ denotes solvent composition. Nonlinear mixed-solvent effects then emerge geometrically as the *shape* of these trajectories: asymmetric dissolution corresponds to skewed mappings in x, cooperative cosolvency to concave (∩-shaped) trajectories, and competitive cononsolvency to convex (∪-shaped) trajectories with suppressed solvation at intermediate compositions. In this view, non-additivity is not an exception to be explained away, but a natural consequence of how dissolution pathways deform in a learned state space.

Within this representation, nonlinear mixed-solvent effects emerge naturally from the geometry of the learned trajectories. Asymmetric dissolution corresponds to skewed mappings in composition space, cooperative cosolvency to concave trajectories, and competitive cononsolvency to convex trajectories with suppressed solvation at intermediate compositions. Because solvents are embedded through continuous descriptors, chemically related solvents induce smooth and directionally consistent deformations of these trajectories, enabling rationalisation of dissolution trends under systematic solvent substitution. By treating binary-solvent dissolution as a structured dynamical process rather than a static compatibility problem, this work provides a unified representation for organising and interpreting complex mixed-solvent behaviour. More broadly, it illustrates how data-driven representation learning can expose low-dimensional structure in non-equilibrium soft-matter systems where additive models fail.

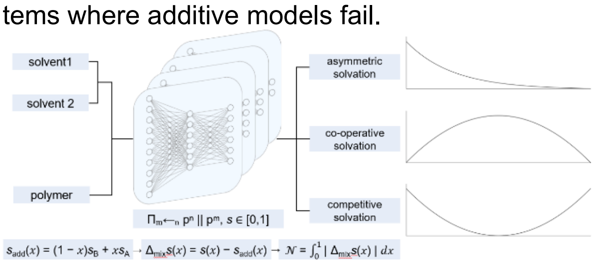

Fig. 1 | Overview of the trajectory-aware ordinal ensemble model for modelling nonlinear binary solvent polymer disssolution effects.

2. Results and Discussion

Polymer dissolution is governed by the Gibbs free energy of mixing, $\Delta G_{mix} = \Delta H_{mix} – T\Delta S_{mix}$, which reflects a balance between enthalpic polymer-solvent interactions and entropic penalties associated with chain connectivity and conformational constraints (Fig. 1). In practical non-ideal polymer systems, these contributions span multiple length and time scales and are difficult to resolve analytically, particularly across diverse chemistries and temperature ranges. Experimentally, polymer–solvent systems are commonly characterised through observable solvation outcomes attained under standardised conditions.

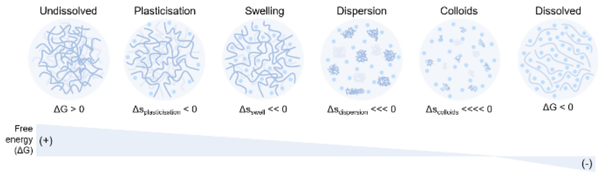

Fig. 2 | Visualisation of ordinal ladder of polymer solvation states.

Aided by high-throughput experimentation [6], we systematically observe asymmetric, cooperative, and competitive dissolution behaviours across a broad polymer–solvent chemical space. Representative examples are shown to illustrate each archetype: asymmetric dissolution in poly(ethylene oxide) (100 kDa) with pyridine and diethylene glycol monomethyl ether (Fig. 2a), cooperative cosolvency in poly(methacrylate) (540 kDa) with 1-octanol and cyclohexanone (Fig. 2b), and competitive cononsolvency in poly(acrylic acid) (450 kDa) with tetrahydrofuran and dimethylacetamide (Fig. 2c). These systems highlight the prevalence of non-additive dissolution pathways and motivate a unified, state-based description of mixed-solvent polymer dissolution.

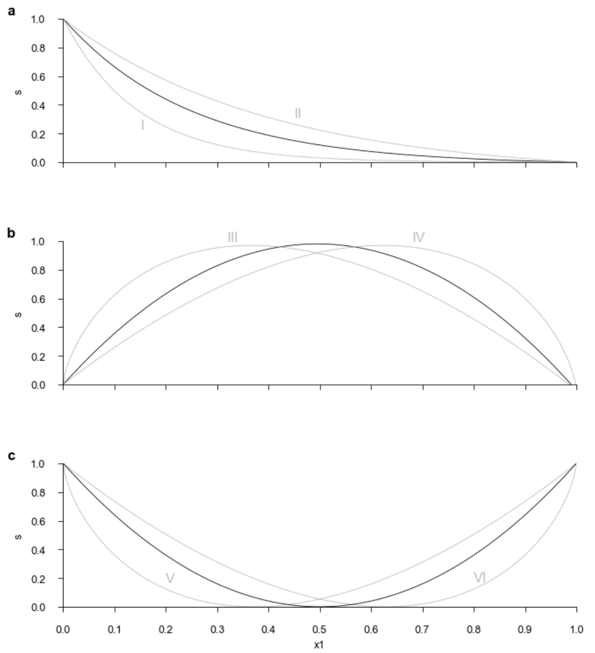

Fig. 3 | Archetypal nonlinear dissolution trajectories in polymer–mixed-solvent systems. a, Asymmetric dissolution arising from unequal solvation strength of the two pure solvents, producing distinct decay pathways. **b,** Cooperative cosolvency, characterised by skewed and ∩-shaped trajectories in which mixed solvents enable dissolution despite neither component being a good solvent individually. **c,** Competitive cononsolvency, manifested as skewed ∪-shaped trajectories where dissolution in pure solvents is suppressed at intermediate compositions.

Data-driven solvation trajectories reveal continuous yet strongly non-additive behaviour as solvent composition varies. By learning a continuous solvation coordinate, mixed-solvent behaviour is expressed as structured trajectories rather than isolated outcomes, allowing asymmetric, cooperative, and competitive effects to be compared within a common framework. Importantly, this representation enables rationalisation of solvent substitution within chemically related families. For example, asymmetric behaviour observed in NMP–ethanol mixtures is reflected as a skewed trajectory whose direction and curvature deform smoothly when ethanol is replaced by methanol or higher alcohols, consistent with systematic changes in solvent polarity and hydrogen-bonding capacity (Fig. 2a). Such behaviour does not imply extrapolative discovery, but demonstrates that the learned representation preserves chemical continuity and captures directionally consistent shifts in dissolution dynamics. In this sense, the value of the approach lies not in predicting new solvent combinations a priori, but in organising and interpreting complex mixed-solvent behaviour as trajectories through an ordered solvation state space.

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