Bundling and Gelation: The phases of an array of parallel-aligned polymers with cross-links

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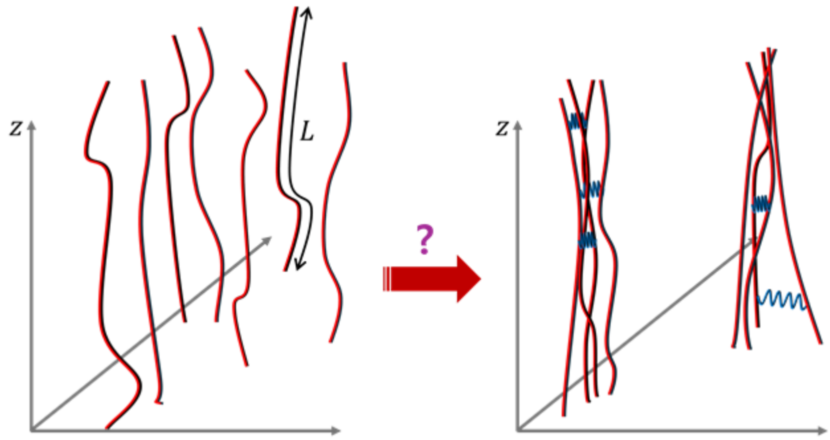
Bundles of parallel-aligned filaments arise in many soft-matter and biological systems when a short-range attraction overcomes a longer-range repulsion, leading to the formation of microstructures. Typical examples include like-charged polymers with short-range attraction mediated by chemical bonds or reversible cross-links. Actin filaments, which are fundamental structural elements of the cytoskeleton, are themselves like-charged and therefore experience electrostatic repulsion. However, actin-binding proteins (ABPs) induce effective shorter-range attractions that give rise to a wide variety of cytoskeletal microstructures, including bundles and networks [1]. In addition, other microscopic mechanisms, such as short-range cation– interactions, have also been shown to promote filament bundling [2,3].

Permanent (chemical) cross-links in a liquid array of parallel-aligned polymers are known to give rise to a nematic gel with a finite in-plane shear modulus [4]. In this context, gelation occurs when the density of permanent cross-links, $\mu^2 = 2[M]/N$ (where M denotes the number of cross-links and N the number of polymers), exceeds unity. At this transition, cross-linked polymers form an infinite, system-spanning percolating cluster in the transverse plane. Since permanent cross-links effectively act as a short-range attractive interaction, they may also promote bundling. However, the role of the cross-link density μ^2 is subtle: while sufficiently strong effective attraction may favor bundling, gelation may occur already at lower cross-link densities, potentially preempting the formation of bundled structures.

Motivated by this competition, we investigate the phase behavior of such systems, with the aim of determining whether they form a gel, bundles, or other distinct phases (Image 1). We treat the permanent cross-links as a quenched disorder described by the Deam–Edwards distribution [5], according to which the probability of a given quenched cross-link configuration follows the annealed statistics of polymer conformations prior to cross-linking. Within this framework, we construct a replica field-theoretic description and derive the corresponding replica free energy. Employing a suitable order parameter implied by a saddle-point approximation, we obtain a Ginzburg–Landau-type free energy that we use to systematically analyze the stability and instabilities of the homogeneous liquid phase.

Our results indicate that when the effective short-range attraction arises solely from spring-like permanent cross-links, these cross-links are not sufficient to induce bundling prior to the onset of gelation. In contrast, in the presence of a sufficiently large fraction of reversible cross-links, permanent cross-links can cooperate with reversible interactions to induce a bundling instability before the gelation transition.



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