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Electrophoresis of a charged polymer attached to an uncharged object: does the nature of the object matter?

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Electrophoresis is the motion of charged objects in a fluid in an electric field. Electrophoretic separation of DNA molecules by length is important in many biomedical applications. It is normally done in a nanoporous medium, such as a gel, since uniformly charged polymers move at the same speed, regardless of their length. This is because such polymers are electrophoretically free-draining, meaning that their parts move in the fluid independently (essentially in "free fall"), with negligible hydrodynamic interactions (HI) between them. Separation by length without a gel becomes possible, if identical neutral objects are attached to the DNA molecules, thus breaking the uniformity. If one still naively assumes free-draining for such composite objects, neglecting HI, then the DNA length dependence of the electrophoretic mobility is predicted to have a universal form, independent of the nature of the object (a linear or branched polymer, a globular protein, a micelle, etc.) and the way it is attached to the DNA, with a single parameter depending only on the hydrodynamic friction coefficient of the object. Taking HI into account in the pre-averaging approximation, we show that, in fact, the form of the length dependence of the electrophoretic mobility depends strongly on the nature of the neutral object and the place of attachment, with, for example, power laws with different exponents observed for short DNA in different cases and a much stronger, exponential dependence when the DNA is attached inside a cavity in a solid object. The mobility can differ by several orders of magnitude for different objects with the same friction coefficient, or even between different attachment points for the same object. Electrostatic analogies help explain some of these cases qualitatively. For a heteropolymer, the electrophoretic mobility is a weighted average of the mobilities of its parts; when an object is attached, the way the weights are modified can be described by an "influence function" that, in many cases, has interesting properties.

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