IUTAM Symposium on 50 Years of Chaos : Applied and Theoretical
Kyoto, Japan, November 28 - December 2, 2011

Geometric approach to the dynamics of charged strings

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Many long molecules may be understood as strands of individual charged units. Generally, the dynamics of such strands depends both on the local elastic deformations of the strand and the nonlocal (screened electrostatic) interactions of charged units across the folds in the molecule. These electrostatic interactions in turn depend on the spatial distances and relative orientations between the individual charged units in different locations along the strand.

Continuum approaches to the dynamics of molecular strands offer an alternative theoretical understanding to the direct numerical simulation of molecular dynamics. One source of this theoretical understanding arises from the recognition of fundamental mathematical properties in the formulation of this dynamics. Many previous studies have addressed the elastic dynamics of the strands using Kirchhoff's approach, which is inherently *local*: the equations of motion are formulated in the system of coordinates that follows all the bends and twists along the strand. Although many important results have been obtained by this approach, it has a limitation. Namely, the generalization of the classical Kirchhoff theory to account for the torque caused by the long-range electrostatic interaction of molecules in different spatial locations along a flexible strand has not been achieved, although the force due to electrostatic interaction has been considered before. This is due to the fact that in order to find the position and orientation of a point on the strand, one needs to find a solution for the strand's configuration, and that in turn is impossible to achieve without knowing Euclidian distance between the points on the strand. It is still possible to find a solution for the *stationary sates* of the non-locally interacting strand using energy minimization techniques in Kirchhoff's approach, but the derivation of the dynamics using classical tools seems difficult, if not impossible.

Our paper introduces a framework that allows treatment of both torques and forces from electrostatic interactions using the *exact geometric theory* of elastic rods. The equations of motion for the dynamical folding of charged molecular strands such as DNA and polymers are derived in the context of flexible continuous filamentary distributions of interacting rigid charge conformations, as shown on Figure 1. The new feature is that the equations of motion for the dynamics of such molecular strands are nonlocal when the screened Coulomb interactions, or Lennard-Jones potentials between pairs of charges (or any other charges depending on the Euclidian distances), are included. These nonlocal dynamical equations are derived using modified Euler-Poincaré and Hamilton-Pontryagin variational formulations that illuminate the various approaches within the framework of symmetry reduction of Hamilton's principle for exact geometric rods [1, 2]. In the absence of nonlocal interactions, the equations recover the classical Kirchhoff theory of elastic rods.

In order to demonstrate a concrete application of our theory, we show how to naturally generate helical molecules and analyze their stability using this geometric approach. We consider an (infinitely) long molecule consisting of repeated conformations of charges, positioned on an elastic backbone, as a model for a polymer like PVDF (polyvinylidene fluoride) polymers. The equations for strands of rigid charge configurations interacting non-locally are formulated on the special Euclidean group, $SE(3)$ representing the rotations and translations of Euclidian space. We show that helical conformations give exact stationary solutions of the equations of motion, and we find and classify all these solutions using energy minimization method. The energy landscape for such a molecule is complex with a large number of energy minima, even when limited to helical shapes. The question of linear stability and selection of stationary shapes is studied using a dynamical $SE(3)$ formulation that naturally accounts for the helical geometry. We investigate the linear stability of a general helical polymer that possesses torque-inducing non-local self-interactions and find the exact dispersion relation for the stability of the helical shapes with an arbitrary interaction potential. We explicitly determine the linearization operators and compute the numerical stability for the particular example of a linear polymer comprising a flexible rod with a repeated configuration of two equal and opposite off-axis charges, thereby showing that even in this simple case the non-local terms can induce instability that leads to the rods assuming helical shapes [3].

Finally, in order to show the prowess of the geometric method, we demonstrate how to apply our theory to the dendronized (dendritic) polymers. These compound molecular structures are formed by assembling multiple dendrimers (a low molecular weight unit to which a number of dendrons, or branches, is attached) that are each connected by its base to a long polymeric backbone. Loosely, these structures can be described as "trees of

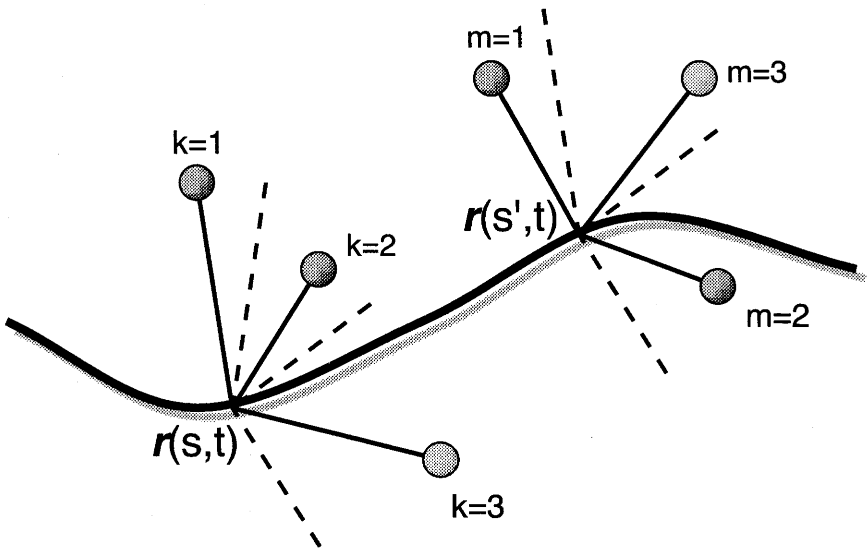

Figure 1: Rigid conformations of charges are distributed along an elastic curve. Such a configuration of charges leads to both forces and torques at each conformation.

charges" on an elastic backbone, and the first patent for synthesizing them was filed in 1987. These structures are playing an ever-increasing role in modern chemistry. While some work has been done in the area using atomistic chain models and Monte-Carlo methods, we are not aware of any previous work capable of describing the *spatio-temporal* evolution of a dendronized polymer. Our geometric approach allows us to formulate the equations of motion for an arbitrary number of "branches" on the "trees", and arbitrary interaction potential between the charges on these "branches" [4].

Acknowledgments

This work is an ongoing collaboration with S. Benoit (CSU), D.C.P.Ellis and D. D. Holm (Imperial), and F. Gay-Balmaz and Tudor Ratiu (EPFL, Lausanne). This work has been partially supported by the National Science Foundation grant NSF-DMS-0908755.

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