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The linking number in systems with Periodic Boundary Conditions

E. Panagiotou

Department of Mathematics, University of California, Santa Barbara, CA 93106, USA

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ABSTRACT

Periodic Boundary Conditions (PBC) are often used for the simulation of complex physical systems. Using the Gauss linking number, we define the periodic linking number as a measure of entanglement for two oriented curves in a system employing PBC. In the case of closed chains in PBC, the periodic linking number is an integer topological invariant that depends on a finite number of components in the periodic system. For open chains, the periodic linking number is an infinite series that accounts for all the topological interactions in the periodic system. In this paper we give a rigorous proof that the periodic linking number is defined for the infinite system, i.e., that it converges for one, two, and three PBC models. It gives a real number that varies continuously with the configuration and gives a global measure of the geometric complexity of the system of chains. Similarly, for a single oriented chain, we define the periodic self-linking number and prove that it also is defined for open chains. In addition, we define the cell periodic linking and self-linking numbers giving localizations of the periodic linking numbers. These can be used to give good estimates of the periodic linking numbers in infinite systems. We also define the local periodic linking number associated to chains in the immediate cell neighborhood of a chain in order to study local linking measures in contrast to the global linking measured by the periodic linking numbers. Finally, we study and compare these measures when applied to a PBC model of polyethylene melts.

1. Introduction

The entanglement of filaments arises in many physical systems, such as polymer melts or fluid flows. The rheological properties of polymer melts are determined primarily by the random-walk-like structure of the constituent chains and the fact that the chains cannot cross [1]. Edwards suggested that entanglements effectively restrict individual chain conformations to a curvilinear tubelike region enclosing each chain [1]. For very short time scales, chain segments are allowed to freely fluctuate in all directions until their displacements become commensurate with the tube diameter, a, which is related to the average distance between entanglements, N_e, by $a^2 = N_e b$, where b is the bond length [2–4]. The axis of the tube is a coarse-grained representation of the chain, called the *primitive path* (PP). Several methods have been developed for extracting the PP network [5–11]. Two geometrical methods capable of efficiently reducing computer generated polymer models to entanglement networks are the Z1-code [7,6,12,13] and the CReTA algorithm [8]. The tube model is very successful and provides a unified view of networks and entangled polymer melts on a mean-field level. Simulations as well as experiments back up the microscopic picture of a tube [14]. Despite these advances, our understanding of entanglement is incomplete

E-mail address: panagiotou@math.ucsb.edu.

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and it is an open question whether these simpler models can be derived from more fundamental topological considerations. The reason is the difficulty to connect the entanglement properties of the chains at two different scales. Indeed, one can distinguish between the local obstacles to the motion of the chains, and the conformational complexity of the entire conformations of the chains in the melt. Similarly, vortex lines in a fluid flow may be seen as mathematical curves that are entangled [15–17]. Helmholtz discovered that the vortex lines move with the fluid in a perfectly inviscid flow [18]. Helmholtz' theorem implied that the global topology of vortex lines remains unchanged throughout the flow evolution. The helicity of a fluid flow confined to a domain D (bounded or unbounded) of three-dimensional Euclidean space $\mathbb{R}^3$ is the integrated scalar product of the velocity field $\vec{u}(\vec{x},t)$ and the vorticity field $\vec{\omega}(\vec{x},t)=\nabla\times\vec{u}$, $H=\int_D \vec{u}\cdot\vec{\omega}dV$ [19,20,15]. Helicity is important at a fundamental level in relation to flow kinematics because it admits topological interpretation in relation to the linking of vortex lines of the flow [15] (see discussion on the linking number in the next paragraph). Invariance of the helicity is then directly associated with invariance of the topology of the vorticity field. Similarly, any solenoidal vector field that is convected without diffusion by a flow will have conserved topology and an associated helicity invariant. Helicity plays a crucial role in the problem of relaxation to magnetostatic equilibrium, a problem of central importance in the context of thermonuclear fusion plasmas [19,16]. Helicity is also related to transition to turbulence [21–23]. When the fluid is conducting, magnetic helicity is an invariant in the ideal case and is central to minimum energy equilibria in plasmas such as in spheromaks, or in solar coronal mass ejections. It is also known that the generation of large-scale magnetic fields occurs due to small-scale mechanic helicity and that in the presence of both rotation and stratification, helicity is created and thus a dynamo is facilitated in a wide variety of astrophysical settings [24,22,25]. Polymer and vortex entanglement share some common features, especially when there is mutual interference, as in the case of polymer solutions. The addition of small amounts of long chain polymers to flowing fluids produces large effects on a wide range of phenomena such as the stability of laminar motion, transition to turbulence, vortex formation and break-up, turbulent transport of heat, mass and momentum, and surface pressure fluctuations [26].

Edwards first pointed out that in the case of ring polymers, the global entanglement of the chains can be studied by using tools from mathematical topology [27,28]. A knot (or link) is one (or more) simple closed curve(s) in space. Knots and links are classified with respect to their complexity by topological invariants, such as knot or link polynomials [29–31]. Since Edwards, many studies have been devoted to the topology of polymer rings and its relation to physical properties [32,5,33–35]. In [34] a direct relation between distinct topological states and N_e has been revealed. However, most of these methods cannot be applied to systems of open chains. The study of global entanglement has been very useful especially in the study of biopolymers [36,37]. Indeed, open curves are not knotted in the topological sense, but they can form complex conformations, which we call *entangled*. Unfortunately, it is not easy to relate intuitive notions of entanglement with topology [38,39]. A classical measure of entanglement that extends naturally to open chains is the Gauss linking integral, *lk*. In the case of closed chains the Gauss linking number is a classical topological integer invariant [40] that is related to the helicity of fluid flows and magnetic fields [41]. More precisely, consider an inviscid incompressible fluid, where the vorticity field is zero except in two closed vortex filaments of strengths (associated circulations) κ_1, κ_2, whose axes are C_1, C_2. Then the *helicity* is $H=2lk(C_1,C_2)\kappa_1\kappa_2$. For pairs of "frozen" open chains, or for a mixed frozen pair, the Gauss linking integral can be applied to calculate an average linking number. For open or mixed pairs, the calculated quantity is a real number that is characteristic of the conformation and changes continuously under continuous deformations of the constituent chains [42]. Thus, the application of the Gauss linking integral to open chains is very clearly not a topological invariant, but a quantity that depends on the specific geometry of the chains. In a similar manner, the Gauss linking integral can be applied to calculate the writhe or the self-linking number of a "frozen" configuration of one open chain. It is true that a complicated tangle and a really untangled curve can have essentially the same writhe, but it takes special effort to construct untangled complicated looking curves with high absolute writhe. Exactly the same considerations apply for the linking number and the self-linking number. Indeed, computer experiments indicate that the linking number and the writhe are effective indirect measures of whatever one might call "entanglement", especially in systems of "random" filaments [41,27,43–48,42,49–54] and it has been shown that they can provide information relevant to the tube model [52,53].

One of the reasons why knots in polymer melts and turbulent flows have not been studied extensively is the problem of handling systems employing PBC [34,55]. Notice that the entire system is created by infinite copies of the simulation cell, and so, applying a traditional measure of entanglement would imply computations involving an infinite number or, at least, a very large number of chains. Furthermore, there exists an infinite number of pairs of chains in the same relative position, giving infinite repetitions of a same pattern. Ideally, one would like to compute a linking measure directly from one cell, but the arcs of the chains inside the cell are relatively short (see Fig. 1). In order to capture the greater degrees of entanglement, or even complex knotting, a large number of arcs must be employed in the creation of a complex chain. In [34,56] the Jones polynomial for systems employing one or two PBC was used to study entanglement in ring polymers. The method presented therein cannot be extended to systems employing 3 PBC. Moreover, the definition of the Jones polynomial is not meaningful when one deals with open chains. In this paper we propose to use the Gauss linking number and its extension to open chains to define a measure of entanglement for chains in one, two or three PBC. This gives a measure of global entanglement of the chains and could be used in the estimation of a topological energy in a system of open, closed or mixed chains with PBC.

In [57], the basis for the study of entanglement in systems employing PBC was introduced, and the *local periodic linking number* was defined and applied to samples of polyethylene (PE) melts. In this paper the *periodic linking number* is defined and its properties for closed, open or infinite chains, and its relation to the Gauss linking number and the local periodic