How to Define Variation of Physical Properties Normal to an Undulating One-Dimensional Object

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One-dimensional flexible objects are abundant in physics, from polymers to vortex lines to defect lines and many more. These objects structure their environment and it is natural to assume that the influence these objects exert on their environment depends on the distance from the line object. But how should this be defined? We argue here that there is an intrinsic length scale along the undulating line that is a measure of its stiffness (i.e., orientational persistence), which yields a natural way of defining the variation of physical properties normal to the undulating line. We exemplify how this normal variation can be determined from a computer simulation for the case of a so-called bottle-brush polymer, where side chains are grafted onto a flexible backbone.

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One-dimensional objects are characteristic for the physics of quite diverse phenomena. Most prominent may be linear polymers [1,2], be they synthetic ones or biopolymers [3], and vortex matter in high T_c superconductors [4,5]. But line objects also determine the characteristics of the structure of (poly-)crystals in the form of defect lines [6] and they were argued to determine the structure of metallic glasses [7] in the form of disclination lines. This list, of course, makes no claim to completeness. In all cases, however, physical properties around the line objects will change depending on distance to the object. For polyelectrolyte chains like, e.g., DNA, one is for instance interested in the distribution of counterions around the chain [8] and the phenomenon of counterion condensation on the (linear) chain. In the case of vortex lines, the order parameter distribution around these lines is important [9], and there exists also a rich phenomenology of interactions between vortex matter and the defect structure of the underlying lattice [10]. It is also well known that dislocation lines in metals control their plastic deformation. Defect lines in ordered materials and the strain fields around them are directly observable in colloidal crystals and nematic materials [11–13] and are of importance for instance for the performance of photonic crystals [14]. In all these cases, physical quantities can be expected to change in space according to the distance of a given point from the line object. Such a normal or radial distance is clearly defined for a straight line, and sometimes one uses models assuming infinite rigidity to look at radial variation, like, for example, the cell model of polyelectrolytes [15], or chain molecules tethered to a straight line as a model for a molecular bottle brush [16], etc. However, the usefulness of all these models has been completely uncertain. In reality these line objects are not infinitely rigid and thus they undulate due to thermal fluctuations. This undulation leads to an interaction between different parts of the lines through the structuring effect they have on their environment. The question of how to define a radial distance from the line object in this case naturally arises when one studies such physical systems with computer simulations, but also for experiments [17], when the structure of a system can be observed for instance microscopically or tomographically.

From the differential geometry of space curves we have an easy answer to this problem locally. Just calculate the two normal vectors (in $3d$) to the line. And globally, when the line object is curled up to a globule or coil, there is no natural normal direction. While the latter is true also when we take into account the granularity of matter, the local definition seizes to be helpful on the atomic scale. Here we will find preferred angles between consecutive segments of the line given either by the underlying chemical nature of the object like in polymers or by an underlying lattice structure like in vortex matter or defect lines. The natural length scale for a definition of normal variation will therefore lie in between this local—and very system specific—and the global—in many cases isotropic—scale. We will discuss in the following how an optimal choice for this intermediate length scale can be identified both in simulations and in experiments providing real space structural information. The procedure will be completely general; however, we will exemplify it for the case of a so-called bottle-brush polymer [16].

Our line object will therefore locally be made out of straight segments—we call them bonds from now on—making up the linear backbone of a bottle-brush polymer shown in Fig. 1. We regard a segment of the backbone of this bottle brush made out of l_c consecutive bonds. For this segment we can define an equivalent cylinder axis as follows: each unit bond vector $\hat{e}_i$ can be seen as the normal to a plane, in which we define cylinder coordinates. The average orientation of these planes is given as

$$\hat{n} = \frac{1}{l_c} \sum_{i=1}^{l_c} \hat{e}_i. \tag{1}$$

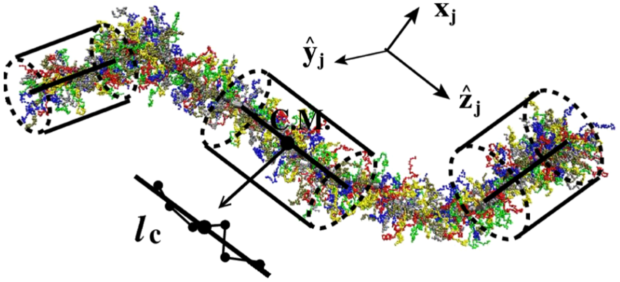

FIG. 1 (color online). Snapshot of a bottle-brush polymer simulated using the bond-fluctuation model. The backbone consists of $N_b = 387$ repeat units and onto each of these a side chain of length $N = 48$ is grafted. One segment of the backbone consisting of l_c bonds is plotted next to the chain. Such segments define a local coordinate system also indicated in the figure and cylinders surrounding the simulated chain as shown (see text).

This definition of $\hat{n}$ is similar to how one would define the normal to an undulating surface. When we assume a triangulation of the surface, each triangle defines a unique normal vector, and the average over these normal vectors for adjacent triangles defines the surface normal on a coarse-grained scale. Using $\hat{n}$ we can define an equivalent straight cylinder for our undulating line on the coarse-grained scale l_c. The z axis is given by $\hat{n}$, it goes through the center of mass (c.m.) of the backbone segment made of $l_c + 1$ monomers and has a length given by the end-to-end distance $R_e^c = \| \vec{r}_{n+l_c} - \vec{r}_n \|$ of the backbone segment between monomers n and $n + l_c$. In the normal plane to this axis we employ cylinder coordinates to define the radial distance of a given point to the axis of the cylinder. Each point in space is considered to count for the normal variation within this cylinder segment, when its z coordinate in the local coordinate frame lies between $z = 0$ and $z = R_e^c$. By construction, each point in space may lie in more than one of these cylindrical segments, in which case it is, however, only counted at the smallest distance to these segments (when degeneracy occurs where a monomer has the same distance to the axis in two cylinder segments, it should be counted for both segments with weight 1/2). Evaluating whichever scalar or tensorial physical property is characteristic for the considered system at these points, one can in this way map out a variation of this property normal to the undulating line for which one performed this construction.

In our case of bottle-brush polymers we study the normal variation of the density of side chain monomers with respect to the backbone of the polymer. This density variation is something one typically tries to extract from scattering experiments [18–21]. Because of unavoidable approximations in the analysis of the scattering data, there has been, however, controversy in the literature [18,19] about the form of this spatial variation. To resolve this controversy we apply our procedure of defining what is meant by variation normal to the backbone of the bottle-brush polymer. Our construction ensures that each monomer is contributing not more than once to the determination of the radial density profile; however, near the backbone chain ends some monomers may not be counted at all (when their z coordinates do not fall into the allowed range for any local cylindrical coordinate system). This is an example of chain end effects occurring whenever the undulating line has only a finite length. The normal variation defined in this way depends on the coarse-graining length scale l_c along the undulating line. Figure 2 shows the dependence of the normal density on this length scale for a backbone of length $N_b = 131$ and side chain length $N = 48$. The data are for a Monte Carlo simulation of the bond-fluctuation lattice model [22]. Clearly, the form of the curves for very small ($l_c = 3$) and very large ($l_c = 130$) values of the coarse-graining length significantly differs from the behavior for intermediate scales. The behavior for small l_c gives comparable results to an approach taken in [23] to measure the counterion concentration around a polyelectrolyte chain. We now want to argue that at the intermediate scales there exists an (almost sharply defined) optimal length scale for coarse graining.

This length scale has to be connected with the intrinsic stiffness of the undulating line object. In polymer physics this is called the persistence length of the polymer chain (here the backbone of the bottle brush). The persistence length is known to be the natural scale for a coarse graining of intramolecular behavior, i.e., variation as a function of chemical distance along the chain. We suggest here, that it is also a natural scale for construction of a coarse-grained description of property variation as a function of spatial distance to the chain. There are several prescriptions of how to obtain the persistence length from an ensemble of

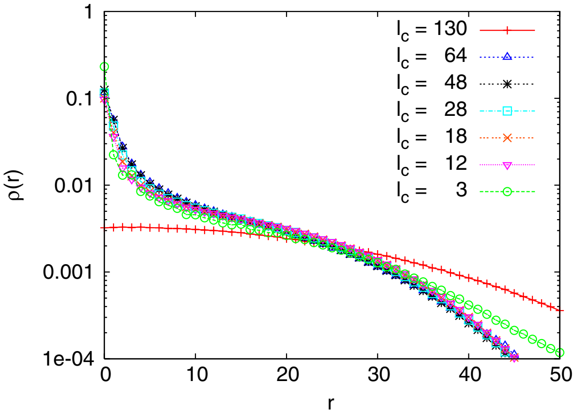

FIG. 2 (color online). Variation of the density of side chain monomers normal to the backbone of the bottle brush for $N_b = 131$ and $N = 48$. Results for several choices of the coarse-graining length l_c along the backbone are shown. All lengths are measured in units of the lattice spacing of the underlying simple cubic lattice.

configurations of a chain. One definition uses the projection of the end-to-end vector of the chain onto the unit bond vector of bond k, measured in terms of the average length of this bond

$$l_p(k) = \langle \vec{b}_k \cdot \vec{R}_e / |\vec{b}_k|^2 \rangle. \tag{2}$$

In a plot of $l_p(k)$ as a function of position k along the chain as shown in Fig. 3 one can clearly identify a plateau regime. The height of this plateau defines the persistence length $l_p^{(1)}$. Another definition employs the bond vector orientational correlation function $\langle \cos\theta(s) \rangle = \langle \hat{e}_i \cdot \hat{e}_{i+s} \rangle$ where the angular brackets include an average over i. For idealized polymer models this function decays exponentially as $a_o \exp\{-s/l_p^{(2)}\}$ (the amplitude prefactor is necessary for discrete models for which the exponential does not extrapolate to one for $s \rightarrow 0$). In reality, this function generally is not a single exponential, and we propose to define the persistence length for arbitrary undulating lines as

$$l_p^{(2)} = \frac{1}{a(N_b - 1)} \sum_{s=1}^{N_b - 1} \langle \cos\theta(s) \rangle. \tag{3}$$

If $l_p^{(2)} \gg 1$ and the decay of $\langle \cos\theta(s) \rangle$ with s is a single exponential, one can for $N_b \rightarrow \infty$ transform the sum to an integral and obtain again the standard definition of $l_p^{(2)}$. It must be noted, however, that for real polymer chains (which have excluded volume interactions) one finds power law decays rather than exponential decay for $N_b \rightarrow \infty$ [24–26]. For isolated self-avoiding walks (good solvent conditions) $\langle \cos\theta(s) \rangle \propto s^{2\nu-2}$ and then $l_p^{(2)} \propto l_p^{(1)} \propto N_b^{2\nu-1}$ [24]. In dense melts $\langle \cos\theta(s) \rangle \propto s^{-3/2}$ [25], $l_p^{(2)}$ [Eq. (3)] then is dominated by the behavior for small s, and does not depend on N_b for lager N_b. Thus the use of Eq. (3) requires care. Both estimates of the persistence length agree within 10% with each other and show an increase by a factor of about 4 (see Fig. 3) when we increase the side chain length from $N = 6$ to $N = 48$. This is in excellent agreement with experiment [27] and agrees with simulations in [28] but is a stronger variation than found in [29]. For the present purposes the important point is that the stiffness length scale l_p (and hence the coarse-graining length scale l_c in Fig. 1) can be varied over a wide range, which allows us to assess the validity of our general concepts.

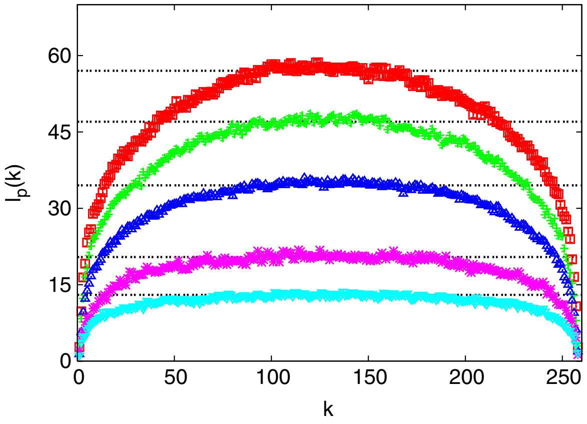

FIG. 3 (color online). Projection of the end-to-end vector of the backbone of the bottle brush onto the local bond orientation as a function of position of the bond along the backbone. The backbone length is $N_b = 259$ and the side chain lengths are $N = 6$, 12, 24, 36 and 48 from bottom to top. Dotted lines indicate values $l_p^{(1)}$ of the persistence length.

When we now take the persistence length as the natural scale for the definition of the coarse-graining length in Fig. 1, i.e. $l_c = l_p$, we find that the normal variation determined in this way is in excellent agreement with what one would determine for a completely rigid backbone. In Fig. 4 we compare the radial density variation for a backbone length $N_b = 131$ and four different side chain lengths $N = 6$, 12, 24, 48 obtained using $l_c = l_p$ to the radial density variation around a rigid backbone [30]. Obviously, our definition of normal variation with respect to the undulating backbone for this choice of coarse-graining length nicely agrees with the variation around the rigid backbone at small to intermediate distances. In this way, we justify the often used rigid backbone model for densely grafted bottle brushes. For large distances, the density measured for a flexible backbone has to be larger than the one measured for the rigid backbone, as the former contains contributions from remote segments of the backbone which can bend back on itself. From our experience, we can vary l_c by about 20% around the choice $l_c = l_p$ without much affecting the agreement observed in Fig. 4. Therefore, the persistence length provides the natural

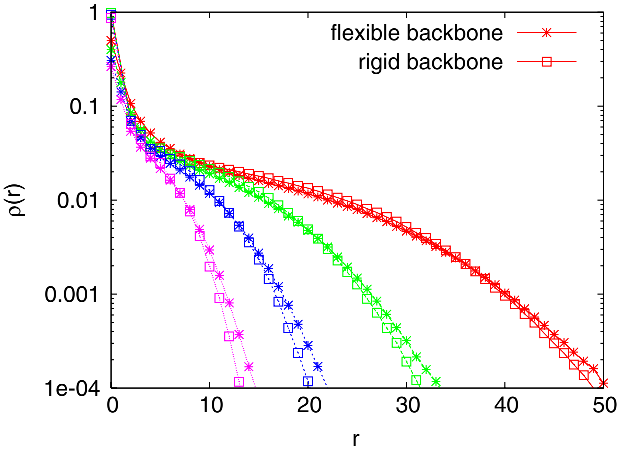

FIG. 4 (color online). Density variation of side chain monomers normal to an undulating backbone of length $N_b = 131$ for the choice $l_c = l_p$ and for the rigid backbone. The four choices of side chain length are $N = 6$, 12, 24 and 48 from left to right.

length scale for the coarse-graining depicted in Fig. 1. Reinterpreting Fig. 4 from a different perspective, we can say that an analysis of the variation of physical properties normal to an infinitely stiff line object gives a good approximation to the behavior for real, thermally fluctuating lines on the scale of the persistence length.

To conclude, we have outlined a constructive procedure on how to define and measure normal variation of physical properties with respect to an undulating line. This problem is relevant for a broad range of physical situations ranging from linear polymers, to vortex matter, to defect lines in crystals. The procedure is applicable for simulations as well as for experiments which provide real space structural information. We explained how a local cylindrical coordinate system can be defined on a coarse-grained scale along the line, in which the normal variation with respect to the undulating line object can then be determined. The optimal length scale for the introduction of cylindrical reference frames turned out to be the persistence length of the fluctuating line object. We showed, for the example of the density variation around the backbone of a bottle-brush polymer, that a normal variation around a flexible backbone determined for this length scale reproduces the normal variation around a rigid backbone on short and intermediate scales, where they should ideally be identical. This example is important, since such stimuli-responsive polymers may find applications as sensors and actuators [31], and for this purpose, as well as for asserting biomolecular functions of bottle brushes such as aggrecane in mammalian joints [32], a deeper understanding of bottle-brush properties is required.

For a reliable interpretation of experimental data on the variation of physical properties around an undulating line object one has to go beyond the approximation of infinite rigidity. This Letter suggests a controlled way to do this and to assess to what extent theoretical descriptions assuming infinite rigidity are valid. Besides the realm of synthetic and biopolymers, we envisage potential applications of our concepts to problems such as the radial distribution of vacancies, solute atoms, etc., around lines in dislocation networks in crystals and liquid crystals. Also, heterogenous nucleation along line defects will be affected by their local curvature and it will be interesting to elucidate the differences to the case of completely rigid defect lines.

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