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Intramolecular distances and form factor of cyclic chains with excluded volume interactions

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Abstract

Numerical simulations are performed for isolated cyclic, or ring, chains with excluded volume. Data are reported for the form factor, $S(x)$, where x is the reduced scattering variable, and also for averages and distributions of the distance between intramolecular units. The averages of distances are compared with two alternative expressions describing their dependence with the number of segments separating the units. The distribution function results are compared with the des Cloizeaux form. Finally the $S(x)$ data are compared with theoretical functions also derived from the des Cloizeaux expression for the distribution function. Moreover, the low x and asymptotic expansions of these functions are obtained. Based on these expansions, simple formulas are proposed to give a good description of the simulation data in the whole range of values of x. A comparison with similar results for linear chains is also included.

Keywords: Cyclic chains; Form factor; Excluded volume

1. Introduction

Both synthetic and natural cyclic polymers are common and important types of molecules [1]. For instance, it is known that DNA may exist in the form of ring molecules. Moreover, the conformational properties of ring chain molecules have a special interest because of their translational invariance along the chain contour. This translational symmetry eliminates the end effects present in linear chains.

The intrachain scattering factor, or form factor, is related to different scattering experiments, and provides a good description of the conformational behavior of chain molecules. The form factor of a flexible polymer chain with N chain units is defined as

$$S(q) = N^{-2} \sum_{j}^{N} \sum_{k}^{N} \left\langle \exp\left[i\boldsymbol{q} \cdot \left(\boldsymbol{R}_j - \boldsymbol{R}_k \right) \right] \right\rangle \tag{1}$$

$\boldsymbol{q}$ is the wavevector that describes the momentum transfer in the scattering, $\boldsymbol{R}_j$ and $\boldsymbol{R}_k$ are the positions of the j-th and k-th chain units and $\langle\rangle$ denotes an equilibrium average over the different orientations and the different conformations of the chain. Although $S(q)$ formally depends on vector $\boldsymbol{R}_j - \boldsymbol{R}_k$ in Eq. (1), a general orientational average shows that the relevant conformational information needed to evaluate the form factor is the distribution of distances between pairs of units [2]. For a long and flexible polymer, the form factor can be expressed in terms of variable $x = q^2\langle S^2 \rangle$, where $\langle S^2 \rangle$ is the mean quadratic radius of gyration of the chain. At very low x, $S(x)$ is similar for all types of chains. However, the form factor behavior is significantly different for different chain models at moderate or large values of x.

The form factor of a long ideal cyclic chain with a Gaussian distribution of intramolecular distances is described by the following equation, derived time ago by Casassa [1,3]:

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$$S(x) = (2/x)^{1/2} e^{-x/2} \int_0^{\sqrt{x/2}} dt\ e^{t^2} \quad (2)$$

This expression is valid for $qb \ll 1$, where b is the length of a polymer unit. This implies not very large x since $\langle S^2 \rangle = Nb^2/12$ for cyclic chains in this particular case of "Gaussian" or "unperturbed" chains [1]. For greater values of q or x, the scattering experiment probes distances for which the structural details of the units are relevant. As long as the restriction $qb \ll 1$ holds, x may have any value from zero to infinity.

However, excluded volume effects have to be introduced in order to describe the general behavior of any isolated long flexible polymer chain immersed in a good solvent [4]. The intrachain distribution function and its averages show large deviations from the Gaussian form, affecting both the average radius of gyration and the form factor. In the case of cyclic chains, deviations from the Casassa function behavior are expected at high x, even for $qb \ll 1$. Some theoretical work has been devoted to give a precise description of $S(x)$. A simple scheme, modifying the intrachain distance form for the averages to take into account excluded volume effects but maintaining their Gaussian distribution, has been proposed by Bensafi et al. [5]. Moreover, a field-theoretical method was applied by Calabrese et al. to obtain the form factor and distribution function of intrachain distances for cyclic chains with excluded volume interactions [6]. This description provides complex formulas and shows that the form of the distribution function is similar to that of the generic function previously proposed for a linear chain with excluded volume by Mazur et al. [7] and des Cloizeaux [8,9] (see below).

Actually, the case of linear chains has received considerable attention. Time ago, Mazur et al. [7] calculated $S(x)$ for linear chains with excluded volume at high x by using an empirical form for both the mean quadratic intramolecular distances between units and the end-to-end distance distribution function. The results were not completely satisfactory since the distribution of intramolecular distances does not have exactly the same functional form as the end-to-end distance distribution function. Renormalization group and scaling theory has been applied to the calculation of distribution functions of distances. The result in three dimensions can be conveniently written in the des Cloizeaux form [8,9] which is formally equivalent to the function employed by Mazur et al.,

$$P(R_{jk}) = K^{\theta+3} \left(R_{jk} / \left\langle R_{jk}^2 \right\rangle^{1/2} \right)^{\theta} \times \exp\left[- \left(K R_{jk} / \left\langle R_{jk}^2 \right\rangle^{1/2} \right)^{t} \right] \frac{t \left\langle R_{jk}^2 \right\rangle^{-3/2}}{4\pi \Gamma[(3+\theta)/t]} \quad (3)$$

where $t = 1/(1-\nu)$ and K is a normalization constant

$$K = \{ \Gamma[(5+\theta)/t] / \Gamma[(3+\theta)/t] \}^{1/2} \quad (4)$$

and $\Gamma(a)$ is the Gamma function.

Parameter ν is actually a critical exponent, whose value is $\nu = 0.588$ [4]. Assuming that both units j and k are in the interior part of the chain (as it is always the case in cyclic chains) the numerical value $\theta = 0.71 \pm 0.05$ is also obtained [8]. In previous work [10] we have shown that the behavior of $S(x)$ can be obtained from the approach of Mazur et al. but performing the conformational average with the des Cloizeaux form of the distribution function, Eq. (3). The expression derived for $S(x)$ (an integral) is in good agreement with experimental and simulation data. Low x and also asymptotic expansions are simply obtained from this approach and these expansions are in total agreement with those previously derived using different mathematical approaches [11,12]. The asymptotic limit together with the low x expansion provide Padé approximants that, with a small number of coefficients, are able to describe the exact integral with small error up to the value of x where a few terms of the asymptotic expansion also give good accuracy.

In this work we study the form factor of cyclic chains both from the numerical and theoretical points of view. We provide simulation data for long chains and, extending the theoretical work that we have previously employed for linear chains, we derive an expression for $S(x)$. With this end, we have to make assumptions on the precise form of the distribution function and averages of the intrachain distances in a cyclic ring. These conformational properties are also obtained from our simulations. The comparison of the theoretical expressions with the simulation data of these conformational properties is, therefore, particularly useful to evaluate the validity of the different assumptions needed to obtain $S(x)$.

2. Numerical simulations

The model and Monte Carlo algorithms used in our simulations have been described and justified in previous work. The chains have N units joined by means of N flexible connectors whose variable lengths follow a Gaussian distribution with root mean square b (b is adopted as the length unit). Non-neighboring units interact through a 6–12 Lennard–Jones potential, characterized by the distance and energy parameters σ and ε (the energy unit is the Boltzmann factor $k_B T$). We set the values $\sigma = 0.8$ at any temperature–solvent condition. The good solvent or excluded-volume conditions are set with the choice $\varepsilon = 0.1$, reproducing the correct behavior in these conditions even for relatively short chains [13].

The algorithm for cyclic chains [14] starts with the generation of a cyclic non-overlapping conformation in a diamond lattice. New conformations are generated from this starting state by choosing two chain units i and j and calculating the two bond vectors $\boldsymbol{v}_i$ and $\boldsymbol{v}_{j+1}$ that connect these units to the longest contour in the cyclic chain. Keeping a constant sum $\boldsymbol{v}_i + \boldsymbol{v}_{j+1}$ we resample each one of the components of $\boldsymbol{v}_i - \boldsymbol{v}_{j+1}$ from a Gaussian distribution with mean equal to zero and mean square deviation $2b^2/3$. This allows us to obtain new positions for units i and j. The shorter path of the chain is rotated by an amount defined by random angle Φ around an axis defined by vector $\boldsymbol{R}_{ij}$ and then translated to connect again