On the behaviour of the short Kratky–Porod chain

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Abstract
Using the exact computation of a large number of moments of the distribution
function of the end-to-end distance $G(r, N)$ of the worm-like chain, we have
established the analytical form of the coefficients in Taylor expansions of the
moments for short chain lengths N. The knowledge of these coefficients
enabled us to resum the moment expansion of $G(r, N)$ by taking into account
consecutively the deviations of the moments from their stiff rod limit. Within
this procedure we have derived the short-chain expansion for $G(r, N)$, the
scattering function, and the extension–force relation, which take into account
the deviations of the moments from their stiff rod limit to the seventh order
in N.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Polymers with contour length L much larger than the persistence length l_p, which is the
correlation length for the tangent–tangent correlation function along the polymer and is a
quantitative measure of the polymer stiffness, are flexible and are described by using the tools
of quantum mechanics and quantum field theory [1–6]. If the chain length decreases, the chain
stiffness becomes an important factor. Many polymer molecules have internal stiffness and
cannot be modelled by the model of flexible polymers developed by Edwards [1].

The standard coarse-graining model of a worm-like polymer was proposed by Kratky and
Porod [7]. The essential ingredients of this model are the penalty for the bending energy and
the local inextensibility. The latter makes the treatment of the model much more difficult.
There have been a substantial number of studies of the Kratky–Porod model in the last half
century [8–18] (see also the references in these cited works). In recent years there has been
increasing interest in the theoretical description of semiflexible polymers [19–29] (see also the
references in these cited works). One reason for this interest is the potential applications of
semiflexible polymers in biology and in research on semicrystalline polymers.

In this paper we present results of a study of the behaviour of the worm-like chain for short lengths. The consideration is based on our recent work [24, 29], where the Fourier–Laplace transform $G(k, p)$ of the end-to-end distribution function $G(r, N)$ (p is the Laplace conjugate of N) was represented as a matrix element of the infinite order matrix $\tilde{P}(k, p) = (I + ikDM)^{-1}D$ with matrices D and M related to the spectrum of the quantum rigid rotator. A truncation of $\tilde{P}(k, p)$ by the matrix of order n gives the end-to-end distribution function $G(k, p)$ as a rational function which is an infinite series in powers of k^2, i.e. it contains all moments of the end-to-end distribution function, and describes the first $2n - 2$ moments exactly. In the context of eigenstates of the quantum rigid rotator, the truncation at order n takes into account the eigenstates with the quantum number of the angular momentum up to the value $l = n - 1$. The moment expansion of $G(k, p)$ can be represented as a double series in powers of k^2 and $1/p$. Alternatively, one can expand $G(k, N)$ in a double series in powers of k^2 and N. Analysing the series of known moments (we have analytically calculated the first 50 moments), we have established that the coefficients in the subseries in powers of k^2 have a simple analytical structure, which enables one to perform a partial resummation of the moment expansion of $G(k, p)$ or $G(k, N)$ (see below). This resummation procedure results in an expansion of $G(r, N)$ around the stiff rod limit, where the end-to-end distribution function is given by the expression $G_r(r, N) = 1/(4\pi N^2)\delta(N - r)$, with the result that, because $G_r(r, N)$ is a distribution, the so-derived short-chain expansion is not a Taylor expansion but rather an expansion in the space of distributions. The knowledge of $G(k, N)$ enables one to compute directly the scattering function $S(k, N)$ and the extension–force relation $R(f)$. In this paper we present the results of a calculation of terms of the short-chain expansions of $G(r, N)$, $S(k, N)$, and $R(f)$ by taking into account the deviations of the moments from their stiff rod behaviour to the seventh order in the chain length N. The procedure can be extended to higher orders. The short-chain expansions, besides having intrinsic interest, can be used for comparisons with approximative treatments, and also in studies of the behaviour of short semiflexible polymers.

The present paper is organized as follows. Section 2 introduces the description of the worm-like chain using the formalism of the quantum rigid rotator. Section 3 explains the idea of the derivation of the short-chain expansion, and presents the short-chain expansions for the distribution function of the end-to-end distance, scattering function, and extension–force relation.

2. The formalism

The Fourier transform of the distribution function of the end-to-end polymer distance of the continuous Kratky–Porod model [7] $G(\mathbf{k}, L) = \int d^3R \exp(-i\mathbf{k}(\mathbf{R} - \mathbf{R_0}))G(\mathbf{R} - \mathbf{R_0}, L)$ is expressed in terms of a path integral as follows:

$$G(\mathbf{k}, L) = \int D\mathbf{t}(s) \prod_s \delta(\mathbf{t}(s)^2 - 1) \exp\left(-i\mathbf{k} \int_0^L ds\, \mathbf{t}(s) - \frac{l_p}{2} \int_0^L ds \left(\frac{d\mathbf{t}(s)}{ds}\right)^2\right), \tag{1}$$

where l_p is the persistence length, and $\mathbf{t}(s) = d\mathbf{r}(s)/ds$ is the tangent vector at the point s along the contour of the polymer. The product over s in equation (1) takes into account that the polymer chain is locally inextensible. In the following the arc length of the polymer L will be measured in units of l_p and will be denoted by N. We now will consider the Green function $P(\theta, \varphi, N; \theta_0, \varphi_0, 0)$ associated with equation (1). The differential equation for P is

$$\frac{\partial}{\partial N} P(\theta, \varphi, N; \theta_0, \varphi_0, 0) - \frac{1}{2}\nabla^2_{\theta,\varphi}P + U(\Omega)P = \delta(N)\delta(\Omega - \Omega_0), \tag{2}$$

where $U(\mathbf{kt}_\Omega) = i\mathbf{kt}_\Omega$ is the potential energy of the rigid rotator in an external field $i\mathbf{k}$, where $\mathbf{k}$ is measured in units of l_p^{-1}. The end-to-end distribution function is obtained from

$P(\Omega, N; \Omega_0, 0)$ as follows:

$$G(k, N) = \frac{1}{4\pi} \int d\Omega \int d\Omega_0 \, P(\Omega, N; \Omega_0, 0). \tag{3}$$

The differential equation (2) can be rewritten as an integral equation as follows:

$$P(\Omega, N; \Omega_0, 0) = P_0(\Omega, N; \Omega_0, 0)$$
$$- \int_0^N ds \int d\Omega' \, P_0(\Omega, N; \Omega', s) U(\mathbf{kt}_{\Omega'}) P(\Omega', s; \Omega_0, 0), \tag{4}$$

where the bare Green function $P_0(\theta, \varphi, N; \theta_0, \varphi_0, 0)$ reads

$$P_0(\theta, \varphi, N; \theta_0, \varphi_0, 0) = \sum_{l,m} \exp\left(-\frac{l(l+1)N}{2}\right) Y_{lm}(\theta, \varphi) Y_{lm}^*(\theta_0, \varphi_0), \tag{5}$$

with $Y_{lm}(\theta, \varphi)$ being the spherical harmonics, and where l and m are the quantum numbers of the angular momentum. Due to the convolution character of expression (4) with respect to the integration over the contour length ($P_0(\Omega, N; \Omega', s)$ depends on the difference $N - s$), the Laplace transform of $P(\Omega, N; \Omega_0, 0)$ in equation (4) with respect to N permits us to get rid of integrations over the contour length. Thus, in the following we will consider the Laplace transform of $G(k, N)$ with respect to N.

It was shown in [24, 29] that the solution of equation (4) results in the following expression for the Fourier–Laplace transform of the end-to-end distribution function as the matrix element of an infinite order square matrix:

$$G(k, p) = \langle 0 | \tilde{P}^s(k, p) | 0 \rangle \tag{6}$$

with

$$\tilde{P}^s(k, p) = (I + ikDM^s)^{-1} D, \tag{7}$$

where the square matrices M^s and D are defined by

$$M_{l,l'}^s = w_l \delta_{l,l'+1} + w_{l+1} \delta_{l+1,l'}, \tag{8}$$

with $w_l = \sqrt{l^2/(4l^2 - 1)}$, and

$$D_{l,l'} = \frac{1}{\frac{1}{2}l(l+1) + p} \delta_{l,l'}, \tag{9}$$

respectively. The superscript s specifies that the quantities $\tilde{P}^s$ and M^s are square matrices. The quantity $\langle 0 | \tilde{P}^s(k, p) | 0 \rangle$ denotes the $(1, 1)$ matrix element of the infinite order square matrix $\tilde{P}^s$. Since the $(1, 1)$ matrix element corresponds to the expectation value of the quantum rigid rotator in the ground state with the quantum number $l = 0$, we prefer to use the above notation. Summations over the magnetic quantum number in the intermediate states in the expression of $G(k, p)$ obtained by solving equation (4) can be eliminated [29], so that summations in the intermediate states occur only over the eigenvalues of the angular momentum $l = 0, 1, \ldots$. This is why the calculation of $G(k, p)$ reduces to the computation of the matrix element of an infinite order square matrix.

The quantity $\tilde{P}^s(k, p)$ plays the key role in the theory, similarly to the bare propagator in common quantum field theories. The end-to-end distribution function $G(k, p)$ is simply the matrix element $\langle 0 | \tilde{P}^s(k, p) | 0 \rangle$, the scattering function of the polymer is the inverse Laplace transform of $G(k, p)/p^2$ multiplied by $2/N$, the partition function of the stretched polymer is $Z(f, N) = G(k = -if/k_B T, N)$, etc [29].

3. The behaviour of a short worm-like polymer

3.1. The idea of the short-chain expansion

To derive the short-chain expansion for the Kratky–Porod chain we insert the expansion of D given by equation (9) according to

$$\frac{1}{\frac{1}{2}l(l+1)+p} = \frac{1}{p}\sum_{m=0}^{\infty}\frac{(-1)^m\,(l(l+1))^m}{2^m}\frac{1}{p^m}$$

into the moment expansion of $G(k, p)$:

$$G(k, p) = \frac{1}{p}\sum_{m=0}^{\infty}(-1)^m\langle 0|(DM^s)^{2m}|0\rangle(k^2)^m, \tag{10}$$

and obtain as a result $G(k, p)$ as a double series in powers of $(k/p)^2$ and $1/p$ as follows:

$$G(k, p) = \sum_{s=1}^{\infty}\frac{1}{p^s}\sum_{n=0}^{\infty}C_n^s\left(\frac{k^2}{p^2}\right)^n. \tag{11}$$

The analysis of 50 exactly computed moments of $G(r, p)$, which are proportional to the coefficients $\langle 0|(DM^s)^{2m}|0\rangle$ in equation (10), shows that the coefficients C_n^s are polynomials in powers of n of the order $2s-3$, i.e. they have the form $C_n^s = a_1 n + a_2 n^2 + \cdots + a_{2s-3}n^{2s-3}$ ($s \geqslant 2$). We determine the coefficients a_i at given s using $2s-3$ known terms of the moment expansion. Further, we test the correctness of the so-obtained C_n^s from comparison with the remaining known terms in the moment expansion, which were not used to determine a_i. The exact knowledge of 50 moments enables one to determine C_n^s for $s \leqslant 11$. The coefficients C_m^s we have obtained in this way are

$$C_n^1 = \frac{1}{2n+1},$$
$$C_n^2 = -\frac{n}{3},$$
$$C_n^3 = \frac{1}{90}n(n+1)(14n+1),$$
$$C_n^4 = -\frac{1}{1890}n(n+1)(2n+3)(62n^2+3n-2),$$
$$C_n^5 = \frac{1}{37\,800}n(n+1)(n+2)(2n+3)(508n^3-84n^2-19n+15),$$
$$C_n^6 = -\frac{1}{3742\,200}n(n+1)(n+2)(2n+3)(2n+5)(10\,220n^4-6236n^3$$
$$\qquad\qquad + 1597n^2+737n-372),$$

$\ldots$

We have also computed the coefficients C_n^7 and C_n^8, but do not write them out here to save space. The determination of higher coefficients demands the knowledge of more moments of the end-to-end distribution function and can be performed in a similar way. After the determination of the coefficients C_n^s we checked the equivalence of (11) with (10) to the corresponding order. Unfortunately, we did not succeed in deriving the expression for the coefficients C_n^s for arbitrary s.

With known coefficients C_n^s one can sum the series over n in (11). Restricting ourselves to the leading order $s_{\max} = 1$ ($s_{\max}$ is the number of terms in the sum over s in (11)) we obtain $G(k, N)$:

$$G_r(k, N) = \frac{\sin(kN)}{kN},$$

and the distribution function of the end-to-end distance:

$$G_r(r, N) = \frac{1}{4\pi N^2} \delta(N - r)$$

in the stiff rod limit. Taking into account the next term in the sum over s in equation (11) gives the correction to the stiff rod limit of the end-to-end distribution function. Thus, the resummation of the moment expansion of $G(k, p)$ according to (11) yields the short-chain expansion for the Kratky–Porod chain.

The above derivation does not allow one to make claims regarding the convergence of the short-chain expansion. The comparison of results of computations of quantities under consideration (for example the scattering function and deformation–force relation) for different $s_{\max}$ gives a criterion determining the quality of the short-chain expansion.

Notice that alternatively one could first carry out the inverse Laplace transformation of (10), and then expand the moments in Taylor series in powers of N. As a result one would arrive at a double series similar to (11) with $1/p$ replaced by N. This makes the meaning of the resummation procedure clearer. To leading order ($s_{\max} = 1$) one replaces the moment by its stiff rod behaviour, $\langle R^{2n} \rangle = N^{2n}$. In next to leading order ($s_{\max} = 2$) one takes into account the next order corrections to the stiff rod behaviour of all moments, and so on.

Due to the fact that the scattering function of the semiflexible polymer $S(k, N)$ is the inverse Laplace transform of $G(k, p)/p^2$ multiplied by the factor $2/N$, the short-chain expansion of $G(k, p)$ enables one to get the short-chain expansion of the scattering function. In fact, Hermans and Ullman [8] derived the stiff rod limit of the scattering function using the stiff rod limit of the moments.

In following subsections we will consider separately the short-chain expansion of the end-to-end distribution function, the scattering function, and the extension–force relation, which can also be obtained from $G(k, N)$.

3.2. Distribution function of the end-to-end distance

The series over n in (11) for known coefficients C_n^s can be easily expressed through the derivatives of the geometric series. Carrying out the inverse Laplace transformation over p gives the short-chain expansion of $G(k, N)$. We have computed $G(k, N)$ by taking into account eight terms in the sum over s in (11), i.e. $s_{\max} = 8$. To save space we present below the result for $s_{\max} = 5$:

$$\begin{aligned}
G_5(k, N) = {} & G_r(k, N) + \frac{1}{6} \frac{\sin(kN)}{k} - \frac{1}{6} N \cos(kN) \\
& + \frac{1}{60} \frac{\sin(kN)\, N}{k} - \frac{7}{360} k \sin(kN)\, N^3 - \frac{1}{60} N^2 \cos(kN) \\
& + \frac{1}{630} \frac{\sin(kN)\, N^2}{k} + \frac{1}{5040} k \sin(kN)\, N^4 - \frac{1}{630} \cos(kN)\, N^3 \\
& + \frac{31}{15\,120} \cos(kN)\, N^5 k^2 + \frac{1}{5040} \frac{\sin(kN)\, N^3}{k} - \frac{1}{5600} k \sin(kN)\, N^5 \\
& + \frac{127}{604\,800} k^3 \sin(kN)\, N^7 \\
& - \frac{1}{5040} \cos(kN)\, N^4 - \frac{53}{151\,200} \cos(kN)\, N^6 k^2.
\end{aligned} \tag{12}$$

The subscript on G and quantities below is $s_{\max}$. Since $G_s(k, N)$ tends to one for $k \to 0$, the end-to-end distribution function is normalized. It is easy to see that the terms in (12) can be represented as derivatives of $\sin(kN)/k$ with respect to N, i.e. of $N G_r(k, N)$. The short-chain expansion of the distribution function of the end-to-end distance is then immediately obtained

from (12) as

$$\pi G_5(r, N) = \frac{1}{4r^2}\delta(N - r) + \frac{1}{12r}\delta(N - r) - \frac{1}{24}\delta^{(1)}(N - r) + \frac{1}{24}\delta(N - r)$$
$$- \frac{r}{30}\delta^{(1)}(N - r) - \frac{7}{1440}r^2\delta^{(2)}(N - r) + \frac{2}{63}r\delta(N - r)$$
$$- \frac{31}{1008}r^2\delta^{(1)}(N - r) - \frac{11}{1440}r^3\delta^{(2)}(N - r) - \frac{31}{60\,480}r^4\delta^{(3)}(N - r)$$
$$+ \frac{5}{144}r^2\delta(N - r) - \frac{37}{1008}r\delta^{(1)}(N - r) - \frac{131}{11\,200}r^4\delta^{(2)}(N - r)$$
$$- \frac{209}{151\,200}r^5\delta^{(3)}(N - r) - \frac{127}{2419\,200}r^6\delta^{(4)}(N - r), \tag{13}$$

where $\delta^{(k)}(x)$ denotes the kth derivative of the Dirac delta function. Note that $G(r, N)$ is a distribution function with respect to r, while the contour length N is a parameter. This should be taken into account in using equation (13) to compute different mean values, for example the moments of the end-to-end distribution function of a short chain. Like the corresponding expansion of the function $\delta_a(x) = 1/(2\pi a^2)^{1/2}\exp(-x^2/2a^2)$ in powers of a, the short-chain expansion of $G(r, N)$ cannot be interpreted as a Taylor series but is rather a generalized Taylor expansion in the space of distributions. The expansions (12), (13) can be used to test approximative expressions of the end-to-end distribution function. We have not succeeded so far in converting the short-chain expansion of the distribution function to a closed expression.

3.3. The scattering function

The scattering function of a semiflexible polymer is defined by

$$S(q, N) = \frac{2}{N}\int_0^N ds_2 \int_0^{s_2} ds_1 \langle\exp(i\mathbf{q}(\mathbf{r}(s_2) - \mathbf{r}(s_1)))\rangle. \tag{14}$$

Expressing $\mathbf{r}(s_2) - \mathbf{r}(s_1)$ in (14) through the tangent vectors, $\mathbf{r}(s_2) - \mathbf{r}(s_1) = \int_{s_1}^{s_2} ds\, \mathbf{t}(s)$, and representing the average in (14) using the formalism of the quantum rigid rotator yields that the scattering function of the semiflexible polymer $S(q, N)$ is the inverse Laplace transform of $G(q, p)/p^2$ multiplied by the factor $2/N$ [24, 29]. Thus, the short-chain expansion of $G(k, p)$ enables one to derive in a straightforward way the short-chain expansion of the scattering function. Taking into account the first four terms in the sum over s in (11) results in the following expression for the scattering function:

$$S_4(x, N)/N = S_r(x)/N + \frac{2}{3}\frac{N}{x^2} - \frac{N\sin x}{x^3} + \frac{1}{3}\frac{N\cos x}{x^2} + \frac{7}{180}\frac{N^2\sin x}{x} + \frac{6}{5}\frac{N^2}{x^4}$$
$$- \frac{13}{15}\frac{N^2\sin x}{x^3} + \frac{4}{15}\frac{N^2\cos x}{x^2} - \frac{6}{5}\frac{N^2\cos x}{x^4} - \frac{32}{63}\frac{N^3}{x^4} + \frac{307}{7560}\frac{N^3\sin x}{x}$$
$$- \frac{125}{126}\frac{N^3\sin x}{x^3} + 3\frac{N^3\sin x}{x^5} + \frac{31}{126}\frac{N^3\cos x}{x^2} - \frac{157}{63}\frac{N^3\cos x}{x^4}$$
$$- \frac{31}{7560}N^3\cos x,$$

where $x = qN$, and

$$S_r(x)/N = 2\frac{\cos(x)}{x^2} - \frac{2}{x^2} + 2\frac{Si(x)}{x}$$

is the scattering function of a stiff rod. The plot of the scattering function multiplied by q for different values of s_{max} is shown in figure 1. The accuracy of the computations is determined by the values of $x = qN$, where curves corresponding to different values of s_{max} begin to diverge. Figure 1 shows that for $N = 1.5$ the continuous and dashed curves begin to diverge for $x \geqslant 9$.
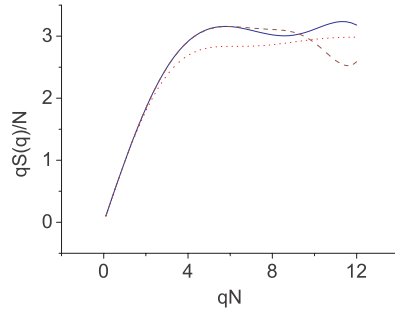
Figure 1. The plot of $qS(q, N)$ for chain length $N = 1.5$. Dots: stiff rod; continuous: $s_{max} = 5$; dashes: $s_{max} = 8$.

3.4. The extension–force relation

The partition function of a semiflexible polymer with one end fixed and force $\mathbf{f}$ applied to the other end,

$$Z(\mathbf{f}, N) = \left\langle \exp\left(-\frac{\mathbf{f}}{k_B T} \int_0^N ds\, \mathbf{t}(s)\right)\right\rangle, \tag{15}$$

can be expressed through the distribution function of the end-to-end distance as follows:

$$Z(\mathbf{f}, N) = G\left(\mathbf{k} = -i\frac{\mathbf{f}}{k_B T}, N\right). \tag{16}$$

Using the definition of the free energy $F = -k_B T \ln Z(f, N)$ the extension–force relation can be expressed through the partition function as

$$R = -\frac{\partial F}{\partial f} = k_B T \frac{\partial \ln Z(f, N)}{\partial f}. \tag{17}$$

Thus, the short-chain expansion of the extension–force relation is directly obtained from that of the Fourier transform of the distribution function of the end-to-end distance (12). Taking into account the first $s_{max} = 4$ terms in the series in (11) results in the following expression for the extension–force relation:

$$\begin{aligned}
\frac{R}{N} = &-\frac{1}{x} + \coth x - \frac{1}{6}Nx - \frac{1}{6}N\coth x + \frac{1}{6}Nx\coth^2 x + \frac{1}{90}N^2\coth x \\
&+ \tfrac{1}{20}N^2 x - \tfrac{1}{36}N^2 x^2 \coth x - \tfrac{7}{180}N^2 x \coth^2 x + \tfrac{1}{36}N^2 x^2 \coth^3 x \\
&- \tfrac{1}{1512}N^3 \coth x + \tfrac{11}{1512}N^3 x^2 \coth x - \tfrac{19}{2520}x N^3 - \tfrac{1}{120}N^3 x^2 \coth^3 x \\
&+ \tfrac{1}{840}N^3 x^3 - \tfrac{11}{1890}N^3 x^3 \coth^2 x + \tfrac{1}{216}N^3 x^3 \coth^4 x + \tfrac{11}{2520}N^3 x \coth^2 x, \tag{18}
\end{aligned}$$

where $x = fN$. The first two terms on the right-hand side of (18) give the extension–force relation for a stiff rod. The log–log plot of $1 - R/N$ for different values of s_{max} and for a stiff rod is shown in figure 2. The slope for the stiff rod is -1, while the slope for the worm-like chain approaches the value $-1/2$, which is the asymptotic result for a finite worm-like chain at large forces [30]. Figure 2 shows that the convergence of the short-chain expansion for the extension–force relation is worse than that of the scattering function.

4. Conclusions

To conclude, using the exact computation of a large number of moments of the end-to-end distribution function $G(r, N)$ of the worm-like chain, which are obtained from
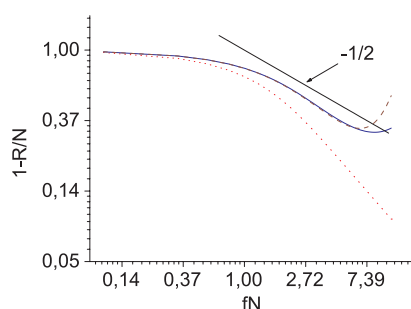
Figure 2. Extension–force relation for chain length $N = 1.1$. Dots: stiff rod; continuous: $s_{max} = 4$; dashes: $s_{max} = 6$.

the representation of the distribution function as the matrix element of the infinite order matrix [24, 29], we have established the analytical form of the coefficients in Taylor expansions of the moments for short N. The knowledge of these coefficients enabled us to resum the moment expansion of $G(r, N)$ by taking into account consecutively the deviations of the moments from their stiff rod limit. Within this procedure we have derived the short-chain expansion for the distribution function of the end-to-end polymer distance, the scattering function, and the extension–force relation, by taking into account the deviations of the moments from their stiff rod limit to the seventh order in N. The procedure can be extended to higher orders. The short-chain expansion could be useful in studies of the behaviour of short polymers, where the deviation from a stiff rod is small.

Acknowledgment

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