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Comment on "General equilibrium shape equations of polymer chains"

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Abstract
In this Comment, we point out that the Euler-Lagrange equations, which are referred to as the general equilibrium shape equations presented by Zhang et al. [Phys. Rev. E 70, 051902 (2004)] are incorrect, along with equations derived from them. The correct equations are provided here and they are cross-checked using certain energy functions previously presented in the literature. Further, with the use of the correct equations, we present new numerical results, which for the values of the constants given by Zhang et al. do not give rise to the physical behavior observed for DNA by those authors. However, the correct equations can be consistent with sensible behavior for different values of the constants.

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Comment on “General equilibrium shape equations of polymer chains”

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In this Comment, we point out that the Euler-Lagrange equations, which are referred to as the general equilibrium shape equations presented by Zhang et al. [Phys. Rev. E 70, 051902 (2004)] are incorrect, along with equations derived from them. The correct equations are provided here and they are cross-checked using certain energy functions previously presented in the literature. Further, with the use of the correct equations, we present new numerical results, which for the values of the constants given by Zhang et al. do not give rise to the physical behavior observed for DNA by those authors. However, the correct equations can be consistent with sensible behavior for different values of the constants.

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To determine the shape of polymer chains, such as proteins and DNA, Zhang et al. [1] adopt a variational principle for an energy density, and obtain in [1] the Euler-Lagrange equations, which are referred to as general equilibrium shape equations. Here, we point out that these equations are incorrect, and we state the correct versions of these equations and those equations derived from them.

For the free energy density $F = F(\kappa(s), \tau(s), \kappa'(s))$, which is a function of the curvature $\kappa(s)$, the torsion $\tau(s)$, and the derivative of the curvature, $\kappa'(s) = d\kappa(s)/ds$, where $s$ is the arclength of the polymer chain, the correct Euler-Lagrange equations are derived by Thamwattana et al. [2], and in a comparable form to those presented by Zhang et al. [1], are given by

$$
\frac{d^2}{ds^2} \left( \frac{2F_\kappa'}{\kappa} + F_\kappa' \right) + \frac{d}{ds} \left( \frac{2F_\kappa'}{\kappa^2} - \frac{3F_\kappa''}{\kappa} \right) + F_\kappa''(\kappa^2 - \tau^2)
$$

$$
+ \frac{d}{ds} \left( 2\kappa \tau - \kappa' \frac{\tau'}{\kappa} + \frac{\tau'}{\kappa^2} \right) - F_\kappa + F_\kappa'(3\kappa \kappa' - 2\tau \tau') - \frac{d}{ds} \left[ F_\kappa'(\kappa^2 - \tau^2) \right] - \frac{d^2}{ds^2} F_\kappa' = 0,
$$

$$
\begin{align*}
\frac{d^2}{ds^2} \left( \frac{F_\kappa'}{\kappa} \right) + \frac{d^2}{ds^2} \left( \frac{F_\kappa'}{\kappa^2} \right) &+ \frac{d}{ds} \left( \frac{F_\kappa'}{\kappa} (\kappa^2 - \tau^2) - 2F_\tau \tau' \right) + F_\tau \tau'

&= 0,
\end{align*}
$$

where $F_\kappa' = \partial F / \partial \kappa$, $F_\kappa' = \partial F / \partial \tau$, and $F_\kappa'' = \partial F / \partial \kappa''$. We note that, for convenience, we adopt the same notation as that in [1], except that here we use only $\kappa' = d\kappa/ds$ and $\tau' = d\tau/ds$, whereas Zhang et al. [1] use both $\kappa'$ and $\kappa''$ to denote $d\kappa/ds$ and $\kappa''$ to represent $d\kappa''/ds$. The incorrect Euler-Lagrange equations given by Zhang et al. [1] originate from Eqs. (2.27) and (2.29) in [1] which are incorrect, and this therefore leads to the mistakes in the Euler-Lagrange equations (2.31) and (2.32) as given in [1]. We comment that the incorrect Eq. (2.27) in Zhang et al. [1] is also employed in another paper by some of the same authors (Zhao et al. [3]).

We refer to Eqs. (B6) and (B7) in Appendix B of Thamwattana et al. [2] for the correct versions of Eqs. (2.27) and (2.29), respectively.

As also shown by Thamwattana et al. [2], Eqs. (1) and (2) can be simplified to yield

$$
\begin{align*}
\frac{d^2}{ds^2} \left( \frac{F_\kappa'}{\kappa} \right) + \frac{d^2}{ds^2} \left( \frac{F_\kappa'}{\kappa^2} \right) &+ \frac{d}{ds} \left( \frac{F_\kappa'}{\kappa} (\kappa^2 - \tau^2) - 2F_\tau \tau' \right) + F_\tau \tau'

&- \frac{d}{ds} \left[ \frac{F_\kappa'(\kappa^2 - \tau^2)}{\kappa} \right] - \frac{d^2}{ds^2} F_\kappa' = 0,
\end{align*}
$$

$$
\begin{align*}
\frac{d^2}{ds^2} \left( \frac{F_\kappa'}{\kappa} \right) + \frac{d^2}{ds^2} \left( \frac{F_\kappa'}{\kappa^2} \right) &+ \frac{d}{ds} \left( \frac{F_\kappa'}{\kappa} (\kappa^2 - \tau^2) - 2F_\tau \tau' \right) + F_\tau \tau'

&- \frac{d}{ds} \left[ \frac{F_\kappa'(\kappa^2 - \tau^2)}{\kappa} \right] - \frac{d^2}{ds^2} F_\kappa' = 0,
\end{align*}
$$

respectively, which are as shown in [4]. We point out that using Eq. (2.32) in Zhang et al. [1] will not result in the second of equations (5), even though they state it correctly in Eq. (3.2) of [1].

For a particular energy density given by

$$
F(\kappa, \tau, \kappa') = \frac{A}{2} \kappa' + \frac{C}{4} \kappa - \frac{\alpha}{2} \kappa^2 \tau + \frac{B}{2} (\kappa^2 + \kappa'^2 \tau) + \lambda.
$$

Zhang et al. [1] claim that substitution of Eq. (6) into their general equilibrium shape equations, which are Eqs. (2.31) and (2.32) in [1], yields the two resultant equations presented by Wei et al. [5], namely,
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\begin{equation}
2A(\kappa^3 - 2\kappa^2 + 2\kappa') - 4\lambda\kappa - 2\alpha(3\kappa^3 - 2\kappa^2 + 6\kappa' - 2\kappa') + 6\kappa'\tau + C(3\kappa^3 - 4\kappa^2 + 24\kappa' + 12\kappa^2\kappa')
+ 2\beta(5\kappa^2 - 2\kappa^2 + \kappa' - 2\kappa\kappa' - 2\kappa''
+ 12\kappa\kappa'\tau + 8\kappa\kappa'\tau - 6\kappa\kappa'\tau - 6\kappa\kappa'\tau)
= 0, \quad (7)
\end{equation}

\begin{equation}
4A(2\kappa' + \kappa - \kappa'' - 2\alpha(6\kappa' + 2\kappa\kappa' - 3\kappa\kappa' - 2\kappa''
+ C(4\kappa^3 + 24\kappa'\kappa + 4\beta(4\kappa' + 6\kappa\kappa' +
- 3\kappa\kappa'\tau - 3\kappa'\tau - 4\kappa'\tau - 2\kappa\kappa'\tau - 2\kappa\kappa'\tau)
= 0. \quad (8)
\end{equation}

This claim is not true, or in other words use of the two general equilibrium shape equations of Zhang et al. [1] does not give rise to Eqs. (7) and (8). By using the correct Eqs. (3) and (4) above, we can verify that by substituting Eq. (6) into Eqs. (3) and (4) we obtain Eqs. (7) and (8) exactly. We note that the constants A, C, -\alpha/2, and \beta are used in [1] correspond, respectively, to the elastic moduli k_2, k_2', k_3, and k_4 shown in [5].

We may further check the two Euler-Lagrange equations Eqs. (3) and (4) by considering the well-known Sadowsky functional [6-8], which has the form

\begin{equation}
F(\kappa, \tau) = \kappa^2(1 + \omega')^2, \quad (9)
\end{equation}

where \omega = \tau/\kappa. We note that the Sadowsky energy function is used to determine the shape of a narrow thin elastic band, such as Möbius strips [6-8]. Upon substituting Eq. (9) into Eq. (4), we obtain

\begin{equation}
2\kappa^3\omega(1 + \omega')\kappa'' + 2(1 + 3\omega^2)\omega'' + [-6\kappa^3\omega(1 + \omega')^2
+ 4\kappa^3(1 + 3\omega^2)\omega'' + 2\kappa^3(1 + 3\omega^2)\kappa'' + 36\omega\omega']\omega''
+ 4\kappa^3\omega(1 + \omega')\kappa' - 4\kappa^2(1 + 3\omega^2)\kappa'\omega''
+ 12\kappa^2\omega\omega'\kappa'' + 12\kappa^2\omega + \kappa(1 + \omega^2)\kappa''
+ \kappa^2(1 + \omega^2)(1 + 3\omega^2)\omega'' = 0, \quad (10)
\end{equation}

which is exactly Eq. (4) in Hangan and Mura [7]. Next, we substitute Eq. (9) into Eq. (3) and obtain

\begin{equation}
2(1 + \omega^2)(1 + 3\omega^2)\kappa'' + 8\omega\omega(1 + 2\omega')(1 + 3\omega^2)\omega''
+ 4\kappa(1 + 9\omega^2)\omega'' - 4\kappa^2\omega^2\omega'' + 4\kappa^2(1 + 3\omega^2)\kappa''
+ \kappa^2(1 + \omega^2)(1 + 2\omega^2)\omega'' = 0. \quad (11)
\end{equation}

By differentiating Eq. (11) with respect to the arclength parameter s, we deduce

\begin{equation}
2(1 + \omega^2)(1 + 3\omega^2)\kappa'' + 8\omega\omega(1 + 2\omega')(1 + 3\omega^2)\omega''
+ [16\omega(2 + 3\omega^2)\omega'' - 8\kappa^2\omega(1 + \omega^2)\kappa'' + [8\kappa^2 + 15\omega^2]\omega''
+ 8\omega(3 + 5\omega^2)\kappa'' + 4\omega(3 + 27\omega^2)\omega'' + 3\kappa^2(1 + 2\omega^2)
\times (1 + \omega^2)\kappa'' + [-8\omega\omega(1 + 2\omega')\kappa'' + 4\kappa\omega(1 + \omega^2)
\times (2 + 3\omega^2)\omega'' + 72\kappa\omega\omega^3 + 4\kappa^2\omega^2(1 + \omega^2)\kappa'' = 0. \quad (12)
\end{equation}

Now we introduce the quantities

\begin{table}
\begin{center}
\begin{tabular}{|c|c|c|c|c|c|}
\hline
DNA & p (nm) & r_0 (nm) & \omega_0 (nm^{-1}) & p/r_0 & r_0/h \\
\hline
A-DNA & 2.46 & 1.3 & 2.55 & 1.89 & 3.32 \\
B-DNA & 3.32 & 1.0 & 1.89 & 3.32 & 1.89 \\
Z-DNA & 4.56 & 0.9 & 1.38 & 5.07 & 1.24 \\
\hline
\end{tabular}
\end{center}
\caption{Helical pitch p and coil radius r_0 of A-, B-, and Z-DNA (Dickerson et al. [9] and Bates and Maxwell [10]), and \omega_0 = 2\pi/p and the relations between p and r_0 and r_0 and h for each type of DNA.}
\end{table}

The parameters \omega_0 = 2\pi/p, \omega_0 = 2\pi/p and the relations between p and r_0 and r_0 and h for each type of DNA are given in Table 1.

\begin{equation}
a = \frac{1}{2\kappa(1 + \omega')}, \quad b = \frac{-\omega}{(1 + \omega')}, \quad c = \frac{\kappa'}{2\kappa(1 + \omega')},
\end{equation}

and it can be shown that the linear combination of (12) + c \times Eq. (10) + c \times Eq. (11) gives rise to

\begin{equation}
kappa''(1 + \omega')\kappa'' + 2\omega\omega'' + [-\kappa'(1 + \omega')^2 + 12\kappa\omega\omega']\kappa''
+ 6\kappa'\omega\omega'' + 8(1 + \omega')^{-1}(1 + 3\omega^2)\omega'' - 8\kappa\kappa'\omega''
+ 8\kappa\omega\omega(1 + \omega')^{-1}(1 + 3\omega^2)\omega'' + 24\omega(1 + \omega')^{-1}\omega''
+ \kappa^2(1 + \omega^2)\kappa'' + 3\kappa^2\omega(1 + \omega^2)\omega'' = 0, \quad (13)
\end{equation}

which is precisely Eq. (3) stated in Hangan and Mura [7].

For the energy density \mathcal{F} of the wormlike chain (WLC) model studied in [1], which depends only on the curvature \kappa, namely

\begin{equation}
\mathcal{F}(\kappa) = \kappa^2 + \lambda, \quad (14)
\end{equation}

where \lambda is a constant representing external forces or constraints, we find from Eq. (5) that we also obtain Eq. (3.7) shown in [1], given by

\begin{equation}
2\kappa' + \kappa'' - \lambda \kappa = 2\kappa'' = 0, \quad C = 4\kappa^2, \quad (15)
\end{equation}

where C denotes an arbitrary constant. Thus, for a coiled polymer chain which has the curvature and torsion given by

\begin{equation}
\kappa = \frac{r_0}{r_0 + h^2}, \quad \tau = \frac{h}{r_0 + h^2}, \quad (16)
\end{equation}

where \tau is the helical coiled radius and h = p/(2\pi), where p is the helical pitch, we deduce from Eq. (15) that

\begin{equation}
r_0^2 - 2h^2 - \lambda (r_0 + h^2)^2 = 0, \quad C = \frac{4\tau^2 h}{(r_0^2 + h^2)}. \quad (17)
\end{equation}

We note that the first of equations (17) is in agreement with Eq. (3.10) in [1]. In the case of \lambda = 0, we have from the first of equations (17) that \tau = \sqrt{2}h, which then gives rise to \lambda = 8/(27h^2). Since p = 2\pi h, therefore \tau = \sqrt{2} \pi = 4.443. Comparing this to the values for A-, B- and Z-DNA shown in Table 1, we see that the WLC model with no external force or constraint applied gives a crude approximation to only the DNA of Z form.

In Zhang et al. [1], the free energy density for the wormlike rod chain (WLRC) model is also examined, which is given by
where $A$ is the bending rigidity, $C$ is the twist rigidity, and $\omega_0$ denotes the spontaneous twist of the helix given by $\omega_0 = 2\pi/p$, where $p$ is the helical pitch. Since the general equilibrium shape equations (2.31) and (2.32) shown in Zhang et al. [1] are incorrect, Eqs. (3.13)-(3.15) in [1], which result from substituting (18) into Eqs. (2.31) and (2.32), are also incorrect. Here, we derive the correct equilibrium shape equations corresponding to the energy density (18) by using the correct Euler-Lagrange equations (3) and (4). From Eqs. (3), (4), and (18), we obtain

$$A\kappa^2 - \kappa^3[(2A - 3C)\tau^2 + 2C\omega_0\tau + C\omega_0^2] + 2A\kappa^2\kappa' - 4C\kappa\tau\tau' + 2C\kappa(2\tau\tau' + \tau'^2) = 0,$$

$$A(C - \tau'^2 + \kappa^3[(2A - 3C)\tau + C\omega_0] + C\kappa(\tau^2\tau' - \tau'^3) + C\kappa(2\tau\tau' + \kappa'\tau') - 2C\kappa^2\tau' = 0.$$  

Thus, for a coiled polymer chain that has the curvature and torsion given by Eq. (16) we deduce from Eqs. (19) and (20) the following relationship for $r_0$ and $h$:

$$(2A - 3C)h^2 - Ar_0^2 + 2C\omega_0h(r_0^2 + h^2) + C\omega_0^2(r_0^2 + h^2)^2 = 0.$$  

We observe that two of the terms involving the constant $C$ differ from those given in [1]. For the given values of $A$ and $C$ in [1] ($A = 50$ nm and $C = 1.5A$) and using $\omega_0 = 1.89$ nm$^{-1}$ from Table I for B-DNA, as shown in Fig. 1 Eq. (21) gives a completely different physical behavior from that indicated in [1]. Upon comparing Eq. (21) with the behavior of B-DNA, it is very clear that, with these given constants, the WLRC model is not suitable for describing the properties of B-DNA. Furthermore, on using $A = 50$ nm and $C = 1.5A$ but changing the values of $\omega_0$ for different DNA (see Table I), we obtain a similar behavior to that of Eq. (21), which is shown by the solid line of Fig. 1. Thus, we may conclude that the WLRC model with the present constants cannot be used to describe the properties of DNA. However, using values of the constants where $C$ is much smaller than $A$, such as $A = 75$ nm and $C = 0.1$ nm, the correct equation may be used to predict the physical behavior of DNA. In fact, when $C$ is much smaller than $A$, the behavior of Eq. (21) approaches that of $r_0 = \sqrt{2}h$, which is the case for the WLRC model that can be used to approximate the physical behavior of Z-DNA (see Fig. 2).

Next, if we ignore the terms $\omega_0$ in Eq. (18) for which the energy density for the WLRC model reduces to

$$\mathcal{F}(\kappa, \tau) = \frac{A}{2}\kappa^2 + \frac{C}{2}\tau^2,$$

then from Eq. (21) we may obtain

$$(2A - 3C)h^2 - Ar_0^2 = 0,$$

which gives rise to

$$\frac{r_0}{h} = \sqrt{\frac{(2A - 3C)}{A}},$$

assuming that $A$ is greater than zero. Thus, for this model to be sensible, we need the condition that the values of $A$ and $C$ are such that $2A - 3C > 0$ and, since both $A$ and $C$ are positive, we have $0 \leq C/A < 2/3$. Furthermore, by prescribing $\mu = r_0/h$, we have

$$\frac{C}{A} = \frac{(2 - \mu^2)}{3}.$$

Upon substituting the values of $\mu = r_0/h$ for A-, B-, and Z-DNA, which are given in Table I, into Eq. (23), we find...
that \( C/A = -3.007, -0.524, \) and 0.154 for A-, B-, and Z-DNA, respectively. Therefore, we may conclude that the functional form (22) is appropriate only for describing the free energy density of Z-DNA, particularly when \( A \) and \( C \) satisfy \( C/A = 0.154 \).

Further, Zhang et al. [1] also consider the solutions for helical biopolymers by substituting Eq. (16) into Eqs. (7) and (8) [which are Eqs. (4.2) and (4.3) in [1]]. We find that Eq. (4.4) in Zhang et al. [1] is incorrect. The correct equation is given by

\[
Cr_0(4b^4 - 3r_0^4) + 2A(2b^6 + 3r_0^2b^4 - r_0^6) \\
- 2\alpha h(2b^4 - r_0^2h^2 - 3r_0^4) + 2\beta h^2(2h^2 - 5r_0^2) + 4\lambda(r_0^2 + h^2)^3 = 0.
\]

(24)

For the case of no external force or constraint (\( \lambda = 0 \)) and for particular values of the constants, namely, \( A = 50 \text{ nm}^2, C = 60 \text{ nm}^2 \), \( \alpha = 40 \text{ nm}^2 \), and \( \beta = 50 \text{ nm}^2 \), used in [1], we plot Eq. (24) (the solid line) showing the relation between \( r_0 \) and \( h \) in Fig. 3, together with the values of A-, B- and Z-DNA. Again, it is clear from Fig. 3 that with the given constants the above model does not describe the properties of any form of DNA, contradicting the claim made by Zhang et al. [1] that this model can be used for B-DNA. However, one might argue that, by choosing a set of appropriate constants, it may be possible to use this model to describe the features of DNA. For example, choosing \( A = 10 \text{ nm}^2, C = 60 \text{ nm}^2, \alpha = 40 \text{ nm}^2, \) and \( \beta = 1 \text{ nm}^2 \), we find from Fig. 4 that Eq. (24) agrees well with the behavior of Z-DNA. For \( A = 50 \text{ nm}^2, C = 20 \text{ nm}^2, \alpha = 40 \text{ nm}^2, \) and \( \beta = 10 \text{ nm}^2 \), Fig. 4 also shows reasonable agreement between the behavior of Eq. (24) and that of B-DNA.

In summary, this Comment provides the correct Euler-Lagrange equations (3) and (4) which are cross-checked using certain energy functionals for which the resulting Euler-Lagrange equations have been given previously in the literature. We point out that Eqs. (2.27) and (2.29) in Zhang et al. [1] are incorrect, leading therefore to the incorrect Euler-Lagrange equations, namely (2.31) and (2.32) in [1]. We comment that since Eqs. (2.31) and (2.32) in Zhang et al. [1] are incorrect, all those results in [1] that are based on these equations are also incorrect. The correct results are provided here, and we find that for the numerical values of the constants given in [1] the WLRC model does not agree with the behavior of any form of DNA. We find that the free energy density, which arises from setting \( \omega = 0 \) in the WLRC model, can be used to describe the physical behavior of Z-DNA when the constants \( A \) and \( C \) involved are chosen to satisfy \( C/A = 0.154 \). For the energy density model proposed by Wei et al. [5], we discover that Eq. (4.4) in [1] is also incorrect. Again we give the correct equation here, namely, Eq. (24) and we also present new numerical results. With the numerical values of the constants used in Zhang et al. [1] we do not find any agreement between the behavior of the model based on [5] and any form of DNA. However, Eq. (24) may still be used for DNA, if appropriate numerical values of the constants are taken. Finally, although the WLRC model with no external force or constraint can be used as a crude approximation, we do not find that it agrees well with Z-DNA as suggested in [1].

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