

# Statistics of wormlike chains. I. Properties of a single chain

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Functional integrals in quasimomentum space (normal mode analysis) is used to study configurational statistics of wormlike chains (WLCs) and properties of WLCs in an external field, with which various correlation functions are defined and can be expressed in terms of simple analytical forms. From the correlation functions, some statistical properties of WLCs, such as gyration radius and scattering functions, have been obtained. The difference between correlation functions and end to end distance distribution functions are discussed, and by varying a parameter the WLC exhibits crossover from an ideal Gaussian chain to a rodlike chain. © 1997 American Institute of Physics. [S0021-9606(97)50905-6]

## I. INTRODUCTION

Since Edwards proposed the continuum model in 1960's<sup>1</sup> much progress has been made. For the ideal Gaussian chain (IGC), the functional integrals can be solved exactly, for example, the end to end distance distribution (EED) function with contour length  $L$ ,  $G(\mathbf{R};L)$ , and after taking an interaction between different monomers, i.e., the excluded volume, into account, a perturbation expansion as well as the renormalization group method are used to study the configurational statistics of polymer solution. Since the aim of this paper is focused on the wormlike chain, the statistics of the ideal Gaussian chains will not be discussed here but can be found in many review books and articles.<sup>1,2</sup>

The wormlike chain (WLC) model was first proposed by Kratky and Porod (KP)<sup>3</sup> and extended to the continuum model (functional integrals) by Saitô, Takahashi, and Yunoki (STY),<sup>4</sup> and Freed,<sup>5</sup> which is described by the statistical weighting factor,<sup>5</sup>  $p[\mathbf{r}(s)]$ ,

$$p[\mathbf{r}(s)] = A \exp \left\{ -\frac{3}{2l} \int_0^L \left( \frac{\partial \mathbf{r}(s)}{\partial s} \right)^2 ds - \frac{\epsilon}{2} \int_0^L \left( \frac{\partial^2 \mathbf{r}(s)}{\partial s^2} \right)^2 ds \right\} \\ = A \exp \left[ -\frac{3}{2l} \int_0^L \mathbf{u}^2(s) ds - \frac{1}{2} \epsilon \int_0^L \dot{\mathbf{u}}^2(s) ds \right], \quad (1.1)$$

where the polymer chain is described by a continuous curve in three-dimensional space  $\mathbf{r}(s)$ , where  $s$  measures the contour length along the chain,  $0 \leq s \leq L$ ,  $\epsilon$  is a bending elastic coefficient,  $\mathbf{u}(s)$  the differential (tangent) of the curve  $\mathbf{r}(s)$ , i.e.,  $\partial \mathbf{r}(s)/\partial s$ , and  $A$  a normalization constant which is equal to the inverse of the partition function. Although the bending elastic term exists which makes the problem complicated,

many methods were proposed. Using the constraint  $|\mathbf{u}(s)|=1$  which means that the polymer chains cannot be stretched, STY derived a series solution for the tangent distribution function (Green's function),  $G(\mathbf{U}, \mathbf{U}'; L, 0)$ , by solving a differential equation for the spherical harmonics<sup>4</sup> and therefore the truncated approximation will be adopted in real applications. Releasing the constraint  $|\mathbf{u}(s)|=1$  which means the polymer chain can be stretched, Freed, using the method by Feynman,<sup>6</sup> derived fruitful results, for example, the EED and tangent distribution functions (Green's functions)  $G(\mathbf{R}, \mathbf{0}; \mathbf{U}, \mathbf{U}'; L, 0)$  and  $G(\mathbf{U}, \mathbf{U}'; L, 0)$  obtained exactly.<sup>5</sup> Another powerful method is the normal mode analysis<sup>7</sup> which is elaborated in the continuum model.<sup>8</sup> This method is just the functional integrals in momentum space<sup>9</sup> which is often used in the field theory and is a convenient method of studying properties of WLCs. In this paper, this method is further extended to study the properties of WLCs.

For the configurational statistics of WLCs, besides the EED functions another essential quantity is the correlation function (or two-body distribution function, however, if the contour length  $s$  is imaged as time as usual<sup>5</sup>  $C(\mathbf{R}_1, \mathbf{R}_2; s_1, s_2)$  is just the correlation function) which is defined for a uniform system

$$C(\mathbf{R}_1, \mathbf{R}_2; s_1, s_2) \propto \langle \delta(\mathbf{r}(s_1) - \mathbf{R}_1) \delta(\mathbf{r}(s_2) - \mathbf{R}_2) \rangle \\ \propto \langle \delta(\mathbf{r}(s_1) - \mathbf{r}(s_2) - \mathbf{R}) \rangle \propto C(\mathbf{R}; s), \quad (1.2)$$

where  $\mathbf{R} = \mathbf{R}_1 - \mathbf{R}_2$ ,  $s = s_1 - s_2$ ,  $0 \leq s_1, s_2 \leq L$  and  $\langle \dots \rangle$  means the statistical average over various configurations of the chain by functional integrals. Here, it should be stressed that the correlation functions are actually more fundamental than the EED functions for WLCs. As pointed out in Ref. 10, the EED functions cannot completely reflect the properties of the WLC, since the EED function gives the mean end to end distance as  $\langle R^2 \rangle = lL$  in the long chain limit. In order to cal-

culate the statistical properties of WLCs, such as scattering function and Gyration radius, we introduce the correlation function (1.2) from which various physical quantities can be obtained. In this paper, various correlation functions including position as well as orientation (tangent) correlation are derived in terms of simple analytical forms and we prove that the correlation functions are generally not equal to the EED functions for the wormlike chain, and only for the IGC is the correlation function,  $C(\mathbf{R};s)$ , just equal to the EED function,  $G(\mathbf{R};L=s)$ . Therefore, in the calculation of various physical quantities, the correlation functions should be used for WLC rather than the EED functions which is often used in the calculation for IGC. In order to manifest the difference between correlation functions and EED functions, we compare the results obtained from these two function.

In the last two decades, polymer liquid crystals (PLCs) have been developed very quickly in experiment and theory. It is believed many PLCs are composed by the wormlike chains and therefore the wormlike chain model has been used extensively to describe polymer liquid crystals.<sup>11-16</sup> In the hairpin model,<sup>12</sup> it is assumed that the WLC is in a mean field provided by the other chains, then the configurations of WLC can be derived by solving a differential equation or even more the hairpin number can be obtained by computer simulation.<sup>11,13-16</sup> On the other hand, the behaviors of PLCs in a strong external field<sup>17</sup> as well as the properties of PLCs in a nematic solvent<sup>18</sup> are investigated. In this paper, the properties of the WLC in an external field are studied by a statistical method developed here, and the problems on the phase transition are discussed in the following paper.

The organization of this paper is as follows. In Sec. II the functional integrals for WLCs are carried out in the quasimomentum space to obtain various correlation functions. Section III deals with WLCs in an external field and, finally, some properties of WLC are studied in Sec. IV. In the following paper, the self-consistent field theory is use to study many WLCs system as well as the phase transition of the polymer liquid crystals.

## II. CORRELATION FUNCTIONS

### A. Functional integrals in momentum space

Let us consider a polymer chain which is described by a three-dimensional curve  $\mathbf{r}(s)$  with contour length  $L$ , where  $0 \leq s \leq L$ . For convenience, the infinite long chain limit is taken then the normal mode coordinate, i.e., the Fourier transformation of  $\mathbf{r}(s)$ , is obtained as usual<sup>8</sup>

$$\mathbf{r}(s) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \mathbf{f}(k) e^{iks} dk, \quad (2.1)$$

where  $\mathbf{f}(k)$  satisfies the condition  $\mathbf{f}(k) = \mathbf{f}^*(-k)$  because  $\mathbf{r}(s)$  is a real function. Then the statistical weighting factor  $p[\mathbf{f}(k)]$  for an IGC can be written as

$$p_{\text{IGC}}[\mathbf{f}(k)] = A \exp\left(-\frac{3}{2l} \int_{-\infty}^{\infty} k^2 \mathbf{f}^2(k) dk\right) \quad (2.2)$$

and for WLC statistical weighting factor (1.1) is

$$p_{\text{WLC}}[\mathbf{f}(k)] = A \exp\left(-\frac{3}{2l} \int k^2 \mathbf{f}^2(k) dk - (\epsilon/2) \times \int k^4 \mathbf{f}^2(k) dk\right). \quad (2.3)$$

Here, and in the following,  $A$  is a constant which can be determined by normalization and  $\mathbf{f}^2(k)$  means  $\mathbf{f}(k) \cdot \mathbf{f}^*(k)$ . Then any physical quantities can be obtained by the functional integral in the quasimomentum space

$$Q = \int \mathcal{A}[\mathbf{f}(k)] Q[\mathbf{f}(k)] p[\mathbf{f}(k)], \quad (2.4)$$

where  $\int \mathcal{A}[\mathbf{f}(k)]$  is functional integral.

### B. Correlation functions

We now use the above model to calculate the correlation functions. According to Eq. (2.1), we obtain

$$\begin{aligned} & \delta((\mathbf{r}(s) - \mathbf{r}(0)) - \mathbf{R}) \\ &= (1/2\pi)^{-3/2} \int_{-\infty}^{\infty} \exp\left\{i\mathbf{w} \cdot \left[\frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \mathbf{f}(k) \times (e^{iks} - 1) dk - \mathbf{R}\right]\right\} d^3w \end{aligned} \quad (2.5)$$

and the tangents of the curve at the contour positions,  $s$ ,

$$\mathbf{u}(s) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} ik \mathbf{f}(k) e^{iks} dk. \quad (2.6)$$

Then, from Eq. (2.4), the correlation function (1.2) for IGC can be written as

$$\begin{aligned} C_{\text{IGC}}(\mathbf{R}, \mathbf{0}; s, 0) &= \int \mathcal{A}[\mathbf{f}(k)] \delta((\mathbf{r}(s) - \mathbf{r}(0)) - \mathbf{R}) \\ & \quad \times p_{\text{IGC}}[\mathbf{f}(k)] \\ &= \int e^{-i\mathbf{w} \cdot \mathbf{R}} d^3w \int \mathcal{A}[\mathbf{f}(k)] p_{\text{IGC}}[\mathbf{f}(k)] \\ & \quad \times \exp\left(\frac{i}{\sqrt{2\pi}} \mathbf{w} \cdot \int_{-\infty}^{\infty} \mathbf{f}(k) (e^{iks} - 1) dk\right). \end{aligned} \quad (2.7)$$

Using standard methods,<sup>8,9</sup> we obtain

$$\begin{aligned}
C_{\text{IGC}}(\mathbf{R}, \mathbf{0}; s, 0) &= A \int e^{-i\mathbf{w} \cdot \mathbf{R}} d^3 w \\
&\times \exp\left(-\frac{\omega^2 l}{3\pi} \int_{-\infty}^{\infty} \frac{\sin^2(ks/2)}{k^2} dk\right) \\
&= A \int e^{-i\mathbf{w} \cdot \mathbf{R}} d^3 w \exp\left(\frac{-\omega^2 l s}{6}\right) \\
&= A \exp\left(\frac{-3R^2}{2ls}\right), \quad (2.8)
\end{aligned}$$

where  $l$  is the effective segment length. This result indicates that the correlation function has the same form as the EED function for the IGC, i.e., whether or not the two points,  $s_1$  and  $s_2$ , are the ends of the chain, the correlation function is just the EED function. This conclusion is correct only for IGC and it is not right for the other correlation functions as well as WLC (see the following). Therefore, it is necessary to introduce the correlation function for the calculation of a physical quantity.

We now consider the correlation function (1.2) for WLC which is obtained from Eqs. (2.3) and (2.4)

$$\begin{aligned}
C(\mathbf{R}, \mathbf{0}; s, 0) &= \int \mathcal{A}[\mathbf{f}(k)] \delta((\mathbf{r}(s) - \mathbf{r}(0)) - \mathbf{R}) p_{\text{WLC}}[\mathbf{f}(k)] \\
&= A \int e^{-i\mathbf{w} \cdot \mathbf{R}} d^3 w \exp\{-\omega^2 l/6 \\
&\quad \times [s - (\epsilon l/3)^{1/2}(1 - \exp(-s\sqrt{3/\epsilon l}))]\} \\
&= A \exp(-R^2/4a_1), \quad (2.9)
\end{aligned}$$

where

$$a_1 = (l/6)(s - (1/\alpha)[1 - e^{-s\alpha}]), \quad \alpha = \sqrt{3/\epsilon l}, \quad (2.10)$$

which is similar to the EED function obtained by STY and KP (the models they used are different from the one used here) and is completely different from the EED function derived by Freed (his model is the same as the one used here and the respective results are exact). This result exhibits the difference between the correlation and EED function and for the EED function, points  $\mathbf{r}(0)$  and  $\mathbf{r}(L)$  are the ends of the chain, but here they are two arbitrary points on the very long chain. It is also interesting to note that the model will lead to a crossover from the IGC through the WLC, and finally to a Gaussian rodlike chain when the parameter  $\epsilon$  is varied which will be discussed in the following section.

In principle, any correlation function can be obtained analytically and in the following we will discuss some important correlation functions. Let us consider an absorption on a surface, then the polymer chain will have a definite orientation  $\mathbf{U}_0$  at  $\mathbf{r}(s=0)$ , for example, the polymer chain may be perpendicular to the surface. The correlation between  $\mathbf{r}(0)$  and  $\mathbf{r}(s)$  is given by the correlation function,  $C(\mathbf{R}, \mathbf{0}, \mathbf{U}_0; s, 0)$ , i.e., we now consider the correlation function with the contour distance,  $s$ ,  $\mathbf{r}(s) - \mathbf{r}(0) = \mathbf{R}$  and the tangent  $\mathbf{U}_0$  at  $s=0$

$$\begin{aligned}
C(\mathbf{R}, \mathbf{0}, \mathbf{U}_0; s, 0) &= \int \mathcal{A}[\mathbf{f}(k)] \delta((\mathbf{r}(s) - \mathbf{r}(0)) - \mathbf{R}) \\
&\quad \times \delta(\mathbf{u}(0) - \mathbf{U}_0) p_{\text{WLC}}[\mathbf{f}(k)] \\
&= A \int e^{-i\mathbf{w} \cdot \mathbf{R}} d^3 w \int e^{-i\mathbf{w}' \cdot \mathbf{U}_0} d^3 w' \\
&\quad \times \int \mathcal{A}[\mathbf{f}(k)] p_{\text{WLC}}[\mathbf{f}(k)] \\
&\quad \times \exp\left[i \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \mathbf{f}(k) \cdot [\mathbf{w}(e^{iks} - 1) + ik\mathbf{w}'] dk\right] \\
&= A \exp\left[-\frac{R^2 a_2 - 2b_1 \mathbf{R} \cdot \mathbf{U}_0 + U_0^2 a_1}{4(a_1 a_2 - b_1^2)}\right], \quad (2.11)
\end{aligned}$$

where

$$b_1 = (l/12)(1 - e^{-s\alpha}), \quad a_2 = \frac{1}{4\alpha\epsilon}. \quad (2.12)$$

Similarly we consider the tangent correlation function of the chain with the contour distance  $s$  and the tangents  $\mathbf{U}_0$  and  $\mathbf{U}$  at the  $s=0$  and  $s$ , respectively, and the result is

$$\begin{aligned}
C(\mathbf{U}, \mathbf{U}_0; s, 0) &= \int \mathcal{A}[\mathbf{f}(k)] \delta(\mathbf{u}(0) - \mathbf{U}_0) \\
&\quad \times \delta(\mathbf{u}(s) - \mathbf{U}) p_{\text{WLC}}[\mathbf{f}(k)] \\
&= A \exp\left[-\frac{U^2 + U_0^2 - 2e^{-s\alpha} \mathbf{U} \cdot \mathbf{U}_0}{4a_2(1 - e^{-2s\alpha})}\right] \quad (2.13)
\end{aligned}$$

which is also different from the EED tangent distribution derived by Freed. If we consider the situation  $|U| = |U_0| = 1$  (i.e., replace  $U^2$  and  $U_0^2$  by its mean values, see Sec. IV) we have

$$C(\mathbf{U}, \mathbf{U}_0; s, 0) = A \exp\left(-\frac{1 - e^{-s\alpha} \cos(\theta)}{2a_2(1 - e^{-2s\alpha})}\right). \quad (2.14)$$

For the correlation function of the chain with the contour distance  $s$ ,  $\mathbf{r}(s) - \mathbf{r}(0) = \mathbf{R}$  and the tangent  $\mathbf{U}$  at  $s$  we have

$$\begin{aligned}
C(\mathbf{R}, \mathbf{0}, \mathbf{U}; s, 0) &= \int \mathcal{A}[\mathbf{f}(k)] \delta((\mathbf{r}(s) - \mathbf{r}(0)) - \mathbf{R}) \\
&\quad \times \delta(\mathbf{u}(s) - \mathbf{U}) p_{\text{WLC}}[\mathbf{f}(k)] \\
&= A \exp\left(-\frac{R^2 a_2 - 2b_1 \mathbf{R} \cdot \mathbf{U} + U^2 a_1}{4(a_1 a_2 - b_1^2)}\right). \quad (2.15)
\end{aligned}$$

We now consider the correlation function of the chain with the contour distance  $s$ ,  $\mathbf{r}(s) - \mathbf{r}(0) = \mathbf{R}$  and the tangents  $\mathbf{U}_0$  and  $\mathbf{U}$  at  $s=0$  and  $s$ , respectively, and we obtain

$$\begin{aligned}
 C(\mathbf{R}, \mathbf{0}, \mathbf{U}, \mathbf{U}_0; s, 0) &= \int \mathcal{A}[\mathbf{f}(k)] \delta((\mathbf{r}(s) - \mathbf{r}(0)) - \mathbf{R}) \delta(\mathbf{u}(0) - \mathbf{U}_0) \delta(\mathbf{u}(s) - \mathbf{U}) p_{\text{WLC}}[\mathbf{f}(k)] \\
 &= A(\mathbf{U}, \mathbf{U}_0) \exp\left(-\frac{R^2(a_2 + b_2) - 2(\mathbf{U} + \mathbf{U}_0) \cdot \mathbf{R}b_1}{4[a_1(a_2^2 - b_2^2) - 2b_2^2]}\right)
 \end{aligned} \quad (2.16)$$

and

$$\begin{aligned}
 A(\mathbf{U}, \mathbf{U}_0) &= \exp\left(-\frac{(U^2 + U_0^2)(a_1 a_2 - b_2^2) + 2\mathbf{U} \cdot \mathbf{U}_0(b_1^2 - a_1 b_2)}{4[a_1(a_2^2 - b_2^2) - 2b_2^2](a_2 - b_2)}\right),
 \end{aligned} \quad (2.17)$$

where

$$b_2 = a_2 \exp(-s\alpha). \quad (2.18)$$

Finally, it is easy to obtain the orientation distribution function of the tangent  $\mathbf{U}$  at position  $s$

$$\begin{aligned}
 C(\mathbf{U}; s) &= \int \mathcal{A}[\mathbf{f}(k)] \delta(\mathbf{u}(s) - \mathbf{U}) p_{\text{WLC}}[\mathbf{f}(k)] \\
 &= A \exp(-U^2/4a_2)
 \end{aligned} \quad (2.19)$$

which is independent of  $s$  because of translation invariance.

From the above results we can conclude that even though for the IGCs the correlation and distribution functions  $C(\mathbf{R}, \mathbf{0}; s, 0)$  and  $G(\mathbf{R}, \mathbf{0}; s, 0)$  have the same form whether or not the points  $\mathbf{r}(0) = \mathbf{0}$  and  $\mathbf{r}(s) = \mathbf{R}$  are the ends of the chain, for WLCs the correlation functions (2.9), (2.13), and (2.16) are quite different from the EED functions.<sup>5</sup> This conclusion can be explained as follows. Considering the correlation between two monomers with  $\mathbf{r}(0) = \mathbf{0}$  and  $\mathbf{r}(s') = \mathbf{R}$ , for IGC the configurations outside parts with  $s < 0$  and  $s > s'$  will not influence the inner part because of the flexibility of the IGC and only give a constant which can be absorbed into the normalization constants. For WLC this is not the case, i.e., the correlation between the two monomers will be different when the two monomers are the ends of the chain or not. The reason is that the outside part of the chain ( $s < 0$  and  $s > s'$ ) will influence the inner part ( $0 < s < s'$ ) because of the nonflexibility of the WLC. This is why the correlation functions are different from the EED functions. However, when the elastic coefficient  $\epsilon \rightarrow 0$ , the difference between  $C(\mathbf{R}, \mathbf{0}; L, 0)$  and  $C(\mathbf{R}, \mathbf{0}; L, 0)$  will vanish. It is the equivalence between correlation and EED functions that the EED function can be used to calculate various statistical quantities for IGCs. For WLCs, the correlation functions should be used rather than the EED function for the statistical physical quantities. In Sec. IV the differences between them will be compared and discussed by calculating numerically some concrete physical quantities.

### III. WLC IN AN EXTERNAL FIELD

In this section we study the properties of WLC in an external field; such a field may be provided by an electromagnetic field<sup>17</sup> or some anisotropic solvents.<sup>18</sup> Here, by the functional integrals various correlation functions can be obtained exactly for the following external field which is often used everywhere<sup>11,13-16</sup> and originates from the dipole moment possessed by the monomers interacting with the field or the dispersion interaction between molecules<sup>19</sup>

$$V = v_0 P_2(\cos \theta(s)) = v_0((3/2)\cos^2 \theta(s) - 1/2), \quad (3.1)$$

where  $v_0$  is the strength of the interaction dependent on the dipole moment,  $P_2$  the Legendre function, and  $\theta$  the angle between the preferred direction determined by the external field and the monomer axis at the contour length  $s$ . This external potential can be expressed in terms of tangents of the chain as

$$V = v_0 \left[ \frac{3}{2} (\mathbf{u}_0 \cdot \mathbf{u}(s))^2 - \frac{1}{2} \right], \quad (3.2)$$

where  $\mathbf{u}_0$  is a unit vector of the preferred direction of the external field and  $\mathbf{u}(s)$  the tangent of the chain at position  $s$ .

Including this potential, the statistical probability of the configuration can be written

$$\begin{aligned}
 p_{\text{ext}}[\mathbf{f}(k)] &= A p_{\text{WLC}}[\mathbf{f}(k)] \\
 &\times \exp\left[-v_0 \int ((3/2)(\mathbf{u}_0 \cdot \mathbf{u}(s))^2 - 1/2) ds\right],
 \end{aligned} \quad (3.3)$$

where  $A$  is a constant which can be determined by normalization. The constant term in the external field can be absorbed into the normalization constant  $A$ , then we have

$$\begin{aligned}
 p_{\text{ext}}[\mathbf{f}(k)] &= A p_{\text{WLC}}[\mathbf{f}(k)] \times \exp\left[-v_0 \int (3/2)k^2 f_z^2(k) ds\right] \\
 &= A \exp\left[-(3/2l)(1 + v_0 l) \int k^2 f_z^2(k) dk \right. \\
 &\quad \left. - (\epsilon/2) \int k^4 f_z^2(k) dk\right] \exp\left[-(3/2l) \int k^2 f_{xy}^2(k) dk \right. \\
 &\quad \left. - (\epsilon/2) \int k^4 f_{xy}^2(s) dk\right] = p[f_z(k)] p[f_{xy}(k)],
 \end{aligned} \quad (3.4)$$

where the  $z$  axis is selected as the preferred direction of the external field. From the above equation it should be noted that when the potential is negative,  $v_0 l$  should be less than 1 otherwise the chain would be broken. It is also clear from the above equation that the following expression:

$$\frac{1}{l_z} = \frac{1}{l} (1 + v_0 l) \quad (3.5)$$

has a clear physical meaning, i.e.,  $l_z$  has a meaning of an effective monomer length (or persistence length) in the  $z$  direction which will also be discussed in the following sec-

tion. Using the method given above, it is easy to obtain the following two points position and tangent correlation functions:

$$\begin{aligned} C(\mathbf{R}, 0; s, 0) &= \int \mathcal{A}[\mathbf{f}(k)] \delta(\mathbf{r}(s) - \mathbf{r}(0)) - \mathbf{R} p_{\text{ext}}[\mathbf{f}(k)] \\ &= \int \mathcal{A}[f_z(k)] \delta((r_z(s) - r_z(0)) - R_z) p[f_z(k)] \\ &\quad \times \int \mathcal{A}[f_{xy}(k)] \delta((r_{xy}(s) \\ &\quad - r_{xy}(0)) - R_{xy}) p[f_{xy}(k)] \\ &= A \exp(-R_z^2/4a_{1z}) \exp(-R_{xy}^2/4a_{1xy}) \end{aligned} \quad (3.6)$$

and

$$\begin{aligned} C(\mathbf{U}, \mathbf{U}_0; s, 0) &= \int \mathcal{A}[\mathbf{f}(k)] \delta(\mathbf{u}(0) - \mathbf{U}_0) \delta(\mathbf{u}(s) - \mathbf{U}) \\ &\quad \times p_{\text{ext}}[\mathbf{f}(k)] \\ &= A \exp\left[-\frac{U_z^2 + U_{0z}^2 - 2e^{-s\alpha_z} U_z U_{0z}}{4a_{2z}(1 - e^{-2s\alpha_z})}\right] \\ &\quad \times \exp\left[-\frac{U_{xy}^2 + U_{0xy}^2 - 2e^{-s\alpha_{xy}} U_{xy} U_{0xy}}{4a_{2xy}(1 - e^{-2s\alpha_{xy}})}\right], \end{aligned} \quad (3.7)$$

where  $R_x(R_y, R_z)$  and  $U_x(U_y, U_z)$  are the  $x(y, z)$  components of  $\mathbf{R}$  and  $\mathbf{U}$ ,

$$R_{xy}^2 = R_x^2 + R_y^2, \quad U_{xy}^2 = U_x^2 + U_y^2, \quad (3.8)$$

$$a_{1z} = \frac{l_z}{6} [s - (1/\alpha_z)(1 - e^{-s\alpha_z})], \quad (3.9)$$

$$a_{1xy} = \frac{l}{6} [s - (1/\alpha_{xy})(1 - e^{-s\alpha_{xy}})], \quad (3.10)$$

$$a_{2z} = \frac{1}{4\alpha_z\epsilon}, \quad a_{2xy} = \frac{1}{4\alpha_{xy}\epsilon}, \quad (3.11)$$

$$\alpha_z = \sqrt{3/\epsilon l_z}, \quad \alpha_{xy} = \sqrt{3/\epsilon l}, \quad (3.12)$$

where  $l_z$  is given by Eq. (3.5). Similarly, the orientation distribution is given by

$$\begin{aligned} C(\mathbf{U}; s) &= \int \mathcal{A}[\mathbf{f}(k)] \delta(\mathbf{u}(s) - \mathbf{U}) p[\mathbf{f}(k)] \\ &= A \exp\left[-\frac{U_z^2}{4a_{2z}} - \frac{U_{xy}^2}{4a_{2xy}}\right] \end{aligned} \quad (3.13)$$

which is independent of  $s$  since the external field preserves the translational invariance and only breaks the rotational invariance.

Here, the exact correlation functions for WLC in the external field are obtained which will be used in the following section as well as the next paper. Similarly, the other correlation functions can be derived as shown in the above section.

## IV. DISCUSSION AND APPLICATIONS

### A. The average monomer–monomer distance of the WLC

From Eq. (2.9) we obtain the average monomer–monomer distance (MMD) (distinguished from the end to end distance EED) separated by the contour distance,  $s$ , for WLC

$$\langle R^2 \rangle = l(s - (1/\alpha)[1 - e^{-s\alpha}]), \quad (4.1)$$

$$\langle R^4 \rangle = (5/3)l^2(s - (1/\alpha)[1 - e^{-s\alpha}])^2. \quad (4.2)$$

Equation (4.1) is also obtained from Refs. 8 and 10 and differentiate from the average EED obtained by Freed<sup>5</sup>

$$\langle R^2 \rangle = l(L - (1/2\alpha)\tanh(L\alpha)) \quad (4.3)$$

which clearly shows the difference between correlation and EED functions. The difference between Eqs. (4.1) and (4.3) comes from the end effect of the chain. The difference is also noted by Lagowski and Noolandj<sup>10</sup> and, in order to patch up the difference, an additional term describing the end effect is added to the Hamiltonian.

When  $\epsilon \rightarrow 0$ , i.e.,  $\alpha = \sqrt{3/\epsilon l} \rightarrow \infty$  the WLC becomes the ideal Gaussian chain, i.e., the mean MMD and the mean EED become the same by setting  $s = L$

$$\langle R^2 \rangle = lL. \quad (4.4)$$

But when  $\epsilon \rightarrow \infty$ , i.e.,  $\alpha \rightarrow 0$  the mean MMD and EED of WLC give incorrect results and in order to make the model valid, an additional condition of the average length of the chain being  $L$  should be used, i.e., as discussed in detail in Ref. 5, let

$$\int_0^L d\tilde{s} = \int_0^L \langle (\mathbf{u}(s) \cdot \mathbf{u}(s))^{1/2} \rangle ds = L, \quad (4.5)$$

where  $d\tilde{s}$  is differential arc length. Then we will obtain a constraint on the parameters,  $l$  and  $\epsilon$ , by Eq. (2.19)

$$\langle \mathbf{u}^2 \rangle = \int \mathbf{u}^2 G(\mathbf{u}; L) d\mathbf{u} / \int G(\mathbf{u}; L) d\mathbf{u} = 6a_2 = \sqrt{\frac{3l}{4\epsilon}} = 1 \quad (4.6)$$

which is equivalent to

$$l = (4/3)\epsilon. \quad (4.7)$$

The above result means that the parameters  $l$  and  $\epsilon$  are not independent of each other and one of them may be selected as the independent parameter. For example, if  $\epsilon$  is selected as the independent parameter  $l$  will depend on  $\epsilon$  and will have a meaning of an effective monomer length (Kuhn length). Another reasonable constraint can be obtained from  $\langle |\mathbf{u}| \rangle = 1$  which leads to  $l = 3\pi^2\epsilon/16$ . A different result is derived by Freed,<sup>5</sup>  $l = \epsilon/3$  obtained from the end to end tangent distribution function, and in Ref. 10,  $l = (4/3)\epsilon$  is derived by taking a limit on Eq. (2.9).

Substituting Eq. (4.7) into Eq. (4.1) we have

$$\langle \mathbf{R}^2 \rangle = l\{L - (l/2)[1 - e^{-2L/l}]\} \quad (4.8)$$

which is the same as the results of the STY and KP models if we let  $l=1/D$ , therefore  $l$  has a meaning of persistence length (see the following). When  $\epsilon \rightarrow \infty$ , the following result is obtained:

$$\langle \mathbf{R}^2 \rangle = L^2, \quad (4.9)$$

which is just the results of a rodlike polymer. Then when  $\epsilon$  varies from zero to infinity the WLC exhibits the crossover from the IGC to the rodlike polymer chain.

## B. Persistence length of the WLC model

After some calculation we can get the persistence length for the WLC model

$$\bar{l} = \frac{\int R \cos \theta C(\mathbf{R}, \mathbf{0}, \mathbf{U}_0; s, 0) d^3 R d^3 U_0}{\int C(\mathbf{R}, \mathbf{0}, \mathbf{U}_0; s, 0) d^3 R d^3 U_0} = b_1 \langle |\mathbf{U}_0| \rangle / a_2 \quad (4.10)$$

and substituting Eq. (4.7) into this equation we have the persistence length for finite contour distance  $s$

$$\bar{l} = (1/\alpha)(1 - e^{-s\alpha}), \quad (4.11)$$

where  $\alpha$  is given by Eq. (2.10), which is similar to the result of the Porod-Kratky model.<sup>4</sup> Let  $s \rightarrow \infty$ , we obtain

$$\bar{l} = 1/\alpha = (2/3)\epsilon = l/2 \quad (4.12)$$

which can be compared with the STY's result

$$\bar{l} = 1/2D = 2\epsilon. \quad (4.13)$$

The reason for the difference is that in our model the chain can be stretched and the average length of the chain is  $L$ .

## C. The order parameter

Considering an absorption near a surface and if all the chains are perpendicular to the surface the average orientation of the chains will be described by the order parameter  $\bar{S}$  which is defined by

$$\bar{S} = \langle S[\theta(s)] \rangle = \frac{\int ds \int_0^\pi S(\theta) C(\mathbf{U}, \mathbf{U}_0; s, 0) d\theta \sin \theta}{\int ds \int_0^\pi C(\mathbf{U}, \mathbf{U}_0; s, 0) d\theta \sin \theta} \quad (4.14)$$

and

$$S(\theta) = (3/2)\cos^2 \theta - 1/2, \quad (4.15)$$

where  $\theta(s)$  is the angle between the preferred direction, which is taken to be that of  $\mathbf{U}_0$ , and the segment which is located at  $\mathbf{r}(s)$ . In order to solve the above equation, the following approximation is used. We first average the order parameter with fixed  $s$ ,

$$\begin{aligned} \bar{S}(s) &= \frac{\int_0^\pi S(\theta) C(\mathbf{U}, \mathbf{U}_0; s, 0) d\theta \sin \theta}{\int_0^\pi C(\mathbf{U}, \mathbf{U}_0; s, 0) d\theta \sin \theta} \\ &= \frac{\int_0^\pi [(3/2)\cos^2 \theta - 1/2] A(s) e^{-q(s)\cos(\theta)} d\theta \sin \theta}{\int_0^\pi A(s) e^{-q(s)\cos(\theta)} d\theta \sin \theta}, \end{aligned} \quad (4.16)$$

where

$$A(s) = \exp\left(-\frac{U^2 + U_0^2}{4a_2(1 - e^{-2s\alpha})}\right), \quad (4.17)$$

$$q(s) = \frac{e^{-s\alpha} U U_0}{2a_2(1 - e^{-2s\alpha})}. \quad (4.18)$$

If we set  $|\mathbf{U}| = |\mathbf{U}_0| = 1$ , we have

$$\bar{S}(s) = (1 + 3/q^2) - (3/q^2)\coth(q) \quad (4.19)$$

with

$$q(s) = \frac{1}{2a_2[e^{s\alpha} - e^{-s\alpha}]}. \quad (4.20)$$

Finally, after averaging over  $s$ , we obtain

$$\bar{S} = (1/L) \int_0^L \bar{S}(s) ds. \quad (4.21)$$

The numerical calculation exhibits that the order parameter changes from zero to one when  $\epsilon$  varies from zero to infinity.

## D. Gyration radius

The gyration radius is defined as

$$R_G^2 = (1/2L^2) \int_0^L ds \int_0^L ds' \langle (R(s) - R(s'))^2 \rangle \quad (4.22)$$

from which it is clear why the correlation function should be used rather than EED function. Substituting Eq. (4.1) into Eq. (4.22) we obtain

$$\begin{aligned} R_G^2 &= (1/L^2) \int_0^L ds \int_0^s ds' [s - s' - (1/\alpha)(1 - e^{-(s-s')\alpha})] \\ &= Ll/6 - l/2\alpha + (l/L^2\alpha^2)[L - (1 - e^{-L\alpha})/\alpha] \end{aligned} \quad (4.23)$$

and using Eq. (4.7) it can be written as

$$R_G^2 = Ll/6 - l^2/4 + (l^3/4L^2)[L - (1 - e^{-2L/l})/2]. \quad (4.24)$$

When  $\alpha \rightarrow \infty$  Eq. (4.24) becomes

$$R_G^2 = Ll/6 \quad (4.25)$$

which is just the IGC's gyration radius. When  $\alpha \rightarrow 0$  using Eq. (4.7) we have

$$R_G^2 = \alpha L^2/24 = L^2/12 \quad (4.26)$$

which is just the same as the gyration radius for the rodlike polymer. Although  $R_G^2$  is the same as the rodlike polymer, the scattering function has a difference from the rodlike polymer for  $\alpha \rightarrow 0$  which can be seen in the next paragraph. In order to manifest the difference between correlation function and EED function, the average MMD in Eq. (4.22),  $\langle (R(s) - R(s'))^2 \rangle$ , is replaced by the average EED (4.3) and the results are shown in the Fig. 1. From Fig. 1 when  $l \ll L$  the correlation function and EED function give the same results and when  $l \gg L$  the result of the EED function leads to  $R_G^2 = Ll/12$  which is half of IGC (4.25) and far from Eq. (4.26), therefore it cannot lead to the rodlike polymer limit.

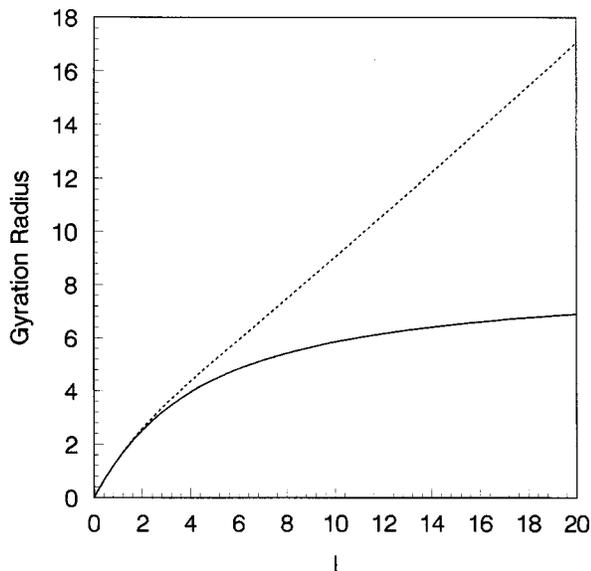


FIG. 1. The gyration radius of WLC with MMD (solid line) and EED (dashed line) versus the effective monomer length  $l$ .  $L=10$  and an arbitrary unit are used here and in the other figures.

### E. Scattering function

The scattering intensity  $I$  is given by<sup>5</sup>

$$I(\theta, \mathbf{U}, \mathbf{U}_0) = A \int_0^L ds C(\mathbf{k}, \mathbf{U}, \mathbf{U}_0; s) \quad (4.27)$$

and its average is given by

$$I(\theta) = A \int_0^L ds \langle C(\mathbf{k}, \mathbf{U}, \mathbf{U}_0; s) \rangle_0 \quad (4.28)$$

where the average,  $\langle \dots \rangle_0$ , means over the orientation,  $|\mathbf{k}| = (4\pi/\lambda)\sin(\theta/2)$ ,  $\theta$  is the scattering angle and  $C(\mathbf{k}, \mathbf{U}, \mathbf{U}_0; L)$  is the Fourier transform of the correlation function

$$C(\mathbf{R}, \mathbf{0}, \mathbf{U}, \mathbf{U}_0; L) = A \int e^{-i\mathbf{k}\cdot\mathbf{R}} d^3k C(\mathbf{k}, \mathbf{U}, \mathbf{U}_0; L). \quad (4.29)$$

This leads to

$$C(\mathbf{k}, \mathbf{U}, \mathbf{U}_0; L)$$

$$= A' \exp\left[-\frac{a_2(U^2 + U_0^2) - 2b_2\mathbf{U}\cdot\mathbf{U}_0}{4(a_2^2 + b_2^2)}\right] \times \exp\left[-k^2\left(a_1 - \frac{2b_1^2}{a_2 + b_2}\right) + i\frac{b_1\mathbf{k}\cdot(\mathbf{U} + \mathbf{U}_0)}{a_2 + b_2}\right]. \quad (4.30)$$

This result is also different from the one derived by the EED function.<sup>5</sup> When  $\epsilon$  is small the difference is very small, but for very stiff chains the difference is much greater.

If we do not consider the distribution of orientation, using Eq. (2.9) we have

$$C(k; L) = \exp\left\{-\frac{k^2 l}{6}\left[L - (\epsilon l/3)^{1/2}(1 - e^{-L\sqrt{3\epsilon l}})\right]\right\}. \quad (4.31)$$

We now calculate the scattering function for WLC which is

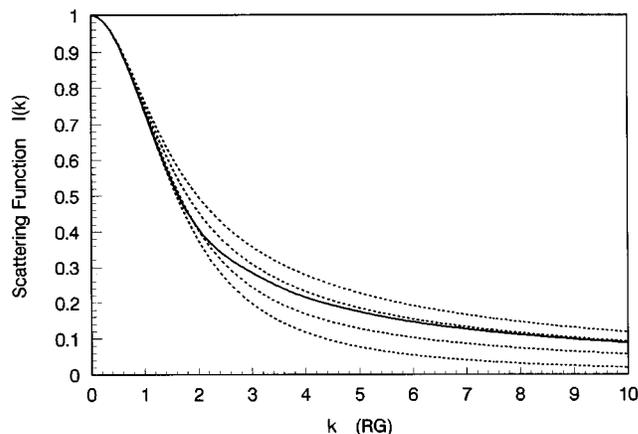


FIG. 2. The scattering functions of WLC and the rodlike polymer (solid line),  $I(x)$  vs  $k$  in the unit  $R_G$  (from the bottom dashed line to the top dashed line): (1) for IGC and WLC with  $L=10$  and  $l=0.01$ ; (2) for WLC with  $L=10$  and  $l=1$ ; (3) for WLC with  $L=10$  and  $l=5$ ; (4) for WLC with  $L=10$  and  $l=100$ .

$$I(k) = (2N/L^2) \int_0^L (L-s) \times \exp\left(-\frac{k^2}{6}l[s - (1 - e^{-s\alpha})/\alpha]\right) ds. \quad (4.32)$$

In order to compare it with the results of the IGC and rodlike polymer, let us write down the scattering function for IGC

$$I(x) = N(2/x^2)(x - 1 + e^{-x}), \quad (4.33)$$

where  $x = k^2 R_G^2$ , and for the rodlike polymer

$$I(x) = L^2(1/6x)[2\sqrt{3x}Si(2\sqrt{3x}) + \cos(2\sqrt{3x}) - 1], \quad (4.34)$$

where

$$Si(x) = \int_0^x (\sin t/t) dt. \quad (4.35)$$

If we let  $\epsilon \rightarrow 0$  ( $\alpha \rightarrow \infty$ ) we find that Eq. (4.32) is just Eq. (4.33). But if we let  $\epsilon \rightarrow \infty$  ( $\alpha \rightarrow 0$ ) and taking into account the condition (4.7) we get

$$I(x) = N \left[ (2/L) \int_0^L \exp(-k^2 x^2/6) dx + (6/k^2 L^2)(e^{-k^2 L^2/6} - 1) \right] \quad (4.36)$$

which cannot lead to Eq. (4.34). This is why it is said that it is similar to the rodlike polymer for  $\epsilon \rightarrow \infty$  in the above paragraph even though it can give the gyration radius of the rodlike polymer. If considering the density distribution, we can also find the difference between the WLC and the rodlike polymer. So we may call this model as Gaussian rodlike polymer when  $\epsilon \rightarrow \infty$ . Figure 2 shows the scattering intensities,  $I(k)$ , for different parameters from which we have seen that when  $L=10$  and  $l=0.01$  the scattering intensity of the WLC is the same as that of the IGC and when  $L=10$  and  $l=5$  the intensity of the WLC is similar to that of the rodlike polymer for large  $k$ . Finally, if the average MMD,

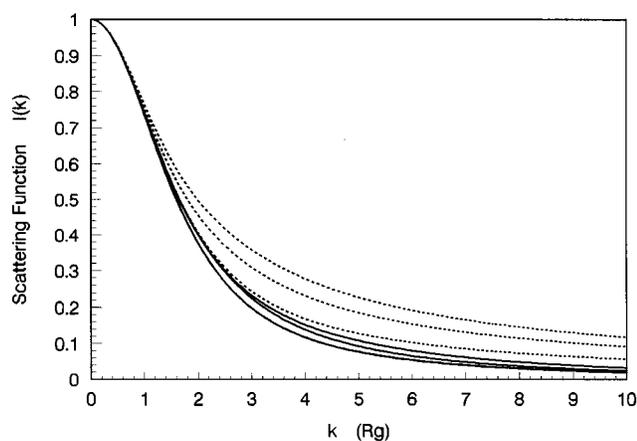


FIG. 3. The scattering functions,  $I(k)$ , of WLC derived from the correlation function and the EED function versus  $k$  in the unit  $R_G$ . The results from the correlation function (dashed line) and parameters are the same as that in Fig. 1 and the solid lines are the results from the EED function with  $l=1$ ,  $l=5$  and  $l=100$ . The results from the correlation function with  $l=0.01$  and from EED with  $l=0.01$  and  $l=1$  coincide.

$\langle (R(s) - R(s'))^2 \rangle$  is replaced by the average EED (4.3), the difference between the correlation and EED functions is clearly shown in Fig. 3. The results from the EED function are close to that of IGC and, especially, considering the unit of  $R_G$  (see Fig. 1), used here the difference between the correlation and EED functions is therefore remarkable.

## F. Properties of the chain in the external field

### 1. The constraint of the WLC in the external field

As discussed above (Sec. IV A), the constraint  $\langle \mathbf{u}^2 \rangle = 1$  for the WLC in the external field

$$\langle \mathbf{u}^2 \rangle = \langle u_z^2 \rangle + \langle u_{xy}^2 \rangle = 2a_{2z} + 4a_{2xy} = 1 \quad (4.37)$$

leads to

$$1 + \frac{1}{2} \sqrt{1/(1+v_0l)} = \sqrt{3\epsilon/l}, \quad (4.38)$$

which is a crucial condition and means three parameters  $\epsilon$ ,  $l$ , and  $v_0$  are only two independent.

### 2. Average MMD of the ideal Gaussian chain in the external field

From Eqs. (3.9)–(3.12) for IGC  $\epsilon \rightarrow 0$  (or  $l \rightarrow 0$ ) which means  $\alpha_z$  and  $\alpha_{xy}$  become infinite, the following results are obtained:

$$a_{1z} = \frac{\langle R_z^2 \rangle}{2} = \frac{lL}{6(1+v_0l)} = \frac{l_z L}{6}, \quad (4.39)$$

$$a_{1xy} = \frac{\langle R_x^2 \rangle}{2} = \frac{\langle R_y^2 \rangle}{2} = \frac{lL}{6}, \quad (4.40)$$

therefore, the ratio of the mean MMD (or EED) in parallel and perpendicular to the direction of the external field is given by

$$a_{1z}/a_{1xy} = \frac{\langle R_z^2 \rangle}{\langle R_x^2 \rangle} = \frac{1}{1+v_0l}. \quad (4.41)$$

The above equations mean that for the IGC in the external field the correlation functions (therefore the global shape) of the IGC are nonspherical.

### 3. Mean MMD of the WLC in the external field

For the WLC the correlation functions will also be prolate or oblate depending if the potential is positive or negative and the ratio of the major and minor axes is given by Eqs. (3.9) and (3.10). It is interesting to note that in the limit case  $\epsilon \rightarrow \infty$  we obtain

$$a_{1z} = \frac{\langle R_z^2 \rangle}{2} = \frac{L^2}{2+4\sqrt{1+v_0l}}, \quad (4.42)$$

$$a_{1xy} = \frac{\langle R_x^2 \rangle}{2} = \frac{\langle R_y^2 \rangle}{2} = \frac{L^2\sqrt{1+v_0l}}{2+4\sqrt{1+v_0l}}, \quad (4.43)$$

therefore we obtain

$$\frac{\langle R_z^2 \rangle}{\langle R_x^2 \rangle} = a_{1z}/a_{1xy} = \frac{1}{\sqrt{1+v_0l}}. \quad (4.44)$$

### 4. The orientation order parameter

It is easy to obtain the tangent correlation function

$$\begin{aligned} C(\mathbf{U}; s) &= A \exp\left(-\frac{\cos^2 \theta}{4a_{2z}} - \frac{\sin^2 \theta}{4a_{2xy}}\right) \\ &= A \exp\left(-\cos^2 \theta(0.5 + \sqrt{1+v_0l})\right. \\ &\quad \left.- \sin^2 \theta \frac{(0.5 + \sqrt{1+v_0l})}{\sqrt{1+v_0l}}\right) \\ &= A \exp(a \cos^2 \theta), \end{aligned} \quad (4.45)$$

where the condition  $|\mathbf{U}|=1$  is used and

$$a = (0.5 + \sqrt{1+v_0l}) \left( \frac{1}{\sqrt{1+v_0l}} - 1 \right). \quad (4.46)$$

Then the order parameter of the WLC in the external field is given by

$$\bar{S}_{\text{ext}} = \frac{\int \exp(a \cos^2 \theta) (1/2) (3 \cos^2 \theta - 1) \sin \theta d\theta}{\int \exp(a \cos^2 \theta) \sin \theta d\theta} \quad (4.47)$$

and numerical calculation shows  $\bar{S}_{\text{ext}}$  changes continuously from 1 to  $-0.5$  when  $v_0l$  varies from  $-1$  to  $\infty$ . Figure 4 shows the orientations of WLC on the external field with negative  $v_0$  for different bending elastic constants.

### 5. The effective monomer length

Because of the existing external field, the properties of the chain will generally be anisotropic, and the most inter-

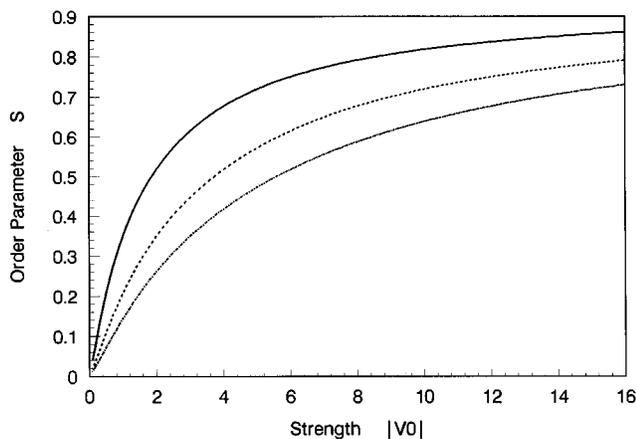


FIG. 4. The order parameter of WLC in an external field,  $S$ , versus the strength of the external field,  $|v_0|$ , for different bending elastic coefficients: solid line for  $\epsilon=3$ , dashed line  $\epsilon=1.5$ , and dash-dotted line  $\epsilon=1$ .

esting one is perhaps the effective monomer length. From intuition, when the external field is negative, i.e.,  $v_0$  negative, the chain will likely be bent in the  $z$  direction which will make the effective monomer length anisotropic. As we know,  $l$  is the effective monomer length (more exactly, the persistence length, see the above) without the external field. When the external field exists, the effective monomer lengths will be anisotropic and have two values,  $l$  and  $l_z$  which are obtained from the following equations:

$$1 + \frac{1}{2} \sqrt{1/(1+v_0 l)} = \sqrt{3 \epsilon / l} \quad (4.48)$$

and

$$l_z = \frac{l}{1+v_0 l} \quad (4.49)$$

for the parameters  $v_0$  and  $\epsilon$ . For negative  $v_0$  the  $l$  changes from zero to  $1/|v_0|$  when  $\epsilon$  varies from zero to infinity and  $l_z$  changes from  $l$  to infinity when  $v_0$  varies from zero to negative infinity. When  $v_0$  is positive, a similar conclusion is easily obtained.

### G. Comparison with the STY model

Before closing this paper we compare the results with that of the STY model<sup>4,5</sup> since the STY model can successfully describe the wormlike chain in many aspects, which can give us more understanding on the WLC. The difference between these two models is that the STY model has the constraint  $|\mathbf{u}| = |\partial \mathbf{r}(s)/\partial s| = 1$ . The main results of the STY model are derived from the following average of the product  $\mathbf{u}(s) \cdot \mathbf{u}(s')$ :

$$\langle \mathbf{u}(s) \cdot \mathbf{u}(s') \rangle = \exp(-|s-s'|/\bar{l}), \quad (4.50)$$

where the persistence length is used,  $\bar{l} = 1/2D = 2\epsilon$ , which can also be calculated by our method

$$\begin{aligned} \langle \mathbf{u}(s) \cdot \mathbf{u}(s') \rangle &= \int \mathcal{A}[\mathbf{f}(k)] \mathbf{u}(s) \cdot \mathbf{u}(s') p_{\text{WLC}}[\mathbf{f}(k)] \\ &= \int \mathbf{u} \cdot \mathbf{u}' C(\mathbf{u}, \mathbf{u}'; s, s') d^3 u d^3 u', \end{aligned} \quad (4.51)$$

where  $C(\mathbf{u}, \mathbf{u}'; s, s')$  is given by Eq. (2.13). With the approximation, Eq. (2.14), i.e.,  $|\mathbf{u}| = |\mathbf{u}'| = 1$ , we can obtain

$$\langle \mathbf{u}(s) \cdot \mathbf{u}(s') \rangle = \coth a - \frac{1}{a}, \quad (4.52)$$

$$\begin{aligned} a &= \frac{\exp(-|s-s'|\alpha)}{2a_2[1 - \exp(-2|s-s'|\alpha)]} \\ &= \frac{3 \exp(-|s-s'|/\bar{l})}{[1 - \exp(-2|s-s'|/\bar{l})]}, \end{aligned} \quad (4.53)$$

where the constraint (4.7) is used for the last equality. After taking limits of  $|s-s'|$  the following results is obtained:

$$\begin{aligned} \langle \mathbf{u}(s) \cdot \mathbf{u}(s') \rangle & \\ \simeq \begin{cases} 1 - \frac{1}{a} \simeq \exp(-2|s-s'|/3\bar{l}), & |s-s'| \ll \bar{l} \\ \frac{a}{3} \simeq \exp(-|s-s'|/\bar{l}), & |s-s'| \gg \bar{l} \end{cases}, \end{aligned} \quad (4.54)$$

which means that for the two segments far from each other these two models are consistent. Although the MMD and EED of STY coincide with  $l = 1/D$  as shown in Eq. (4.8), the fourth moments are different from each other: The result of the STY model

$$\begin{aligned} \langle R^4 \rangle &= \frac{1}{2D^4} \left[ \frac{10}{3} D^2 L^2 - \frac{52}{9} DL + \frac{107}{27} - 4e^{-2DL} \right. \\ &\quad \left. - 2DLe^{-2DL} + \frac{1}{27} e^{-6DL} \right]; \end{aligned} \quad (4.55)$$

the present result

$$\begin{aligned} \langle R^4 \rangle &= \frac{5}{3} l^4 \left[ (L/l)^2 - L/l + \frac{1}{4} - \frac{1}{2} e^{-2L/l} + (L/l) e^{-2L/l} \right. \\ &\quad \left. + \frac{1}{4} e^{-4L/l} \right]. \end{aligned} \quad (4.56)$$

With  $l = 1/D$  they lead to the same limit,  $\langle R^4 \rangle = (5/3)(L/D)^2 = (5/3)(Ll)^2$ , for  $L \gg l$ . All the above results are not strange and can easily be understood since the segments will be uncorrelated when  $|s-s'|$  and  $L \gg l$  which, therefore, leads to the same limits.

However, it should be emphasized that the meanings of the correlation  $\langle \mathbf{u}(s) \cdot \mathbf{u}(s') \rangle$  in these two models are different even though they lead to the same limit when  $L \gg l$ .  $\langle \mathbf{u}(s) \cdot \mathbf{u}(s') \rangle$  is the end to end correlation in STY model, but in our model it is the correlation between two arbitrary segments which are not ends of the chain. Similarly, the other properties can be discussed and we will not go further.

### V. SUMMARY

In this paper, the concept of correlation function for WLCs is proposed. The method of functional integrals in momentum space (normal mode analysis) is used to estab-

lished an exact analytical model for the wormlike chains, and using this model the analytical expressions for various correlation functions of WLCs as well as WLCs in an external field have been obtained. The difference between the correlation and EED functions have been discussed and it is found that for IGC the correlation function  $C_{IGC}(\mathbf{R}, \mathbf{0}; L, 0)$  and EED function  $G_{IGC}(\mathbf{R}, \mathbf{0}; L, 0)$  has the same form whether the points,  $\mathbf{r}(0)=\mathbf{0}$  and  $\mathbf{r}(L)=\mathbf{R}$ , are the ends of the chain or not, and for WLC they have a different form. From the correlation functions some properties of WLC as well as WLC in the external field are studied, for example, the average MMD, gyration radius, and the scatter functions of WLC as well as the orientations of WLC in the external field and the ratio of mean MMDs parallel and perpendicular to the direction of the external field are obtained. Finally, the results obtained here are compared with that of the STY model which gives us more understanding on the wormlike chains. Furthermore, we expect that the WLC gives a good description of main chain polymer liquid crystals which will be discussed in following paper.

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