# The flexible and the wormlike range in a real polymer chain

Giuseppe Allegra

---

---

# The flexible and the wormlike range in a real polymer chain

Giuseppe Allegra

*Istituto di Chimica del Politecnico, Piazza Leonardo da Vinci, 32-20133 Milano, Italy*
(Received 25 January 1983; accepted 26 May 1983)

From the statistics of unperturbed chains with interdependent rotations, a quadratic intramolecular potential of general validity may be derived on the basis of the Fourier configurational representation [G. Allegra, J. Chem. Phys. **68**, 3600 (1978)]. Introducing a suitable observational cutoff it is proven that any real chain shows a different elastic behavior whether $D$ is larger (flexible range) or smaller (wormlike range) than a suitable limit. In the case of polyethylene and atactic polystyrene, the latter range is observable for $D$ smaller than $\sim 25$ Å (and larger and $\sim 8$ Å). The flexible range exists even for the ideal, infinitely long Porod–Kratky chain; its neglect leads to an inconsistency between the intramolecular potential and the mean-square chain length.

## INTRODUCTION

In limiting cases, two alternative expressions in terms of Wiener integrals may be used for the elastic potential of polymer chains[1-3]

$$E = K_a \int^L (\partial R/\partial s)^2 ds \ , \tag{1a}$$

$$E = K_b \int^L (\partial^2 R/\partial s^2)^2 ds \ , \tag{1b}$$

where $R(s)$ is the vector position of the general point having a continuous contour coordinate $s$ ($0 \leqslant s \leqslant L$). While Eq. (1a) is appropriate for a perfectly flexible chain that may be elastically stretched, Eq. (1b) applies to inextensible, stiff chains (the wormlike, or Porod–Kratky model).[4] It is more or less intuitive that one same chain may be reasonably well described with either model, depending on the scale of the observation length. We will show that the configurational statistics of chains with interdependent skeletal rotations[5] provides a theoretical basis for the above models, giving also their limits of validity as well as the parameters $K_a$ and $K_b$.

## TWO ELASTIC RANGES IN A REAL CHAIN

It is well known that the probability $W$ of the end-to-end vector $r$ of a long unperturbed chain

$$r = l(1) + l(2) + \cdots + l(N) \ ; \quad N \to \infty \ , \tag{2}$$

[$l(k)$ is the general chain bond vector] is distributed according to the Gaussian law

$$W(r) = \left(\frac{3}{2\pi \langle r^2 \rangle_0}\right)^{3/2} \exp\left(-\frac{3r^2}{2\langle r^2 \rangle_0}\right) \ , \tag{3}$$

where $r = |r|$ and $\langle r^2 \rangle_0$ stands for its unperturbed configurational average. This result may be justified by considering that, in spite of short-range correlations, $r$ is the sum of terms that are mostly independent in the statistical sense, so that the Central Limit Theorem applies.[6] (Of course, this conclusion fails if the chain is *completely rigid*, so that $\lim_{n \to \infty} \langle l(k) \cdot l(k+n) \rangle \neq 0$.) For the same reason, any linear combination of the $l(k)$'s such as

$$\tilde{l}(q) = \sum_{k=1}^N l(k) \exp(iqk) \quad (q = \text{any real value}) \tag{4}$$

is also Gaussian distributed,[7] i.e.,

$$W(\tilde{l}(q)) = \left(\frac{3}{2\pi \langle l(q) \cdot l(q)^* \rangle_0}\right)^{3/2} \exp\left(-\frac{3\tilde{l}(q) \cdot \tilde{l}(q)^*}{2\langle l(q) \cdot l(q)^* \rangle_0}\right) \ . \tag{5}$$

[Note incidentally that Eq. (3) is implicit in Eq. (5) if we take $q = 0$, because $r = l(0)$.] Restricting now our consideration to the following values of $q$:

$$\{q\} = 0, \pm 2\pi/N, \pm 4\pi/N, \ldots \pi \ , \tag{6}$$

it turns out that the $\tilde{l}(q)$'s constitute an orthogonal set. Consequently, within the Gaussian approximation the chain configurational distribution may be written as

$$W\{\tilde{l}(q)\} = \prod_{\{q\}} W(\tilde{l}(q)) \ , \tag{7}$$

from which the following quadratic intramolecular potential may be obtained[7]:

$$E = -k_B T \ln W\{\tilde{l}(q)\} = E_0 + \frac{3k_B T}{2Nl^2} \sum_{\{q\}} \tilde{l}(q) \cdot \tilde{l}^*(q)/C(q) \ , \tag{8}$$

with the definitions

$$C(q) = \langle \tilde{l}(q) \cdot \tilde{l}^*(q) \rangle_0 / Nl^2 \ ; \quad l = \text{(chain bond length)} \ . \tag{9}$$

In a previous paper, it was shown that the configurational probability given by Eq. (7) leads to a Gaussian distribution for any interatomic distance within the chain, with the correct mean-square value.[8] Since it may be proven that such a distribution is associated with the potential of *fixed forces* producing *average distances* within the quadratic approximation [e.g., see the Appendix, Eq. (A9)], Eq. (8) must be interpreted as the general expression of the intramolecular potential wherein an appropriate set of fixed forces originate the average configurational components $\tilde{l}(q)$.

The function $C(q)$ [Eq. (9)] may be defined as the generalized characteristic ratio because $C(0) = C_\infty$;[5] it is evaluated with the same conformational parameters and mathematical procedures as adopted to obtain the usual characteristic ratio $C_\infty$.[5,7] Although the present results are strictly valid for a chain with an $(\cdots -A-A-A-\cdots)$ structure, they appear to hold for chains with a more general constitution, provided the most localized modes (i.e., those with large $|q|$), as well as some small, fast-relaxing contributions are neglected.[9]

The potential given by Eq. (8) is not in the form of a Wiener integral; however, we will show that it may indeed undergo such a transformation and also that, under

suitable conditions, it may be reduced to either form of Eq. (1). Let us first express the bond vectors $l(k)$ in terms of the components $l(q)$ by antitransforming Eq. (4) [see also Eq. (6)],

$$l(k) = N^{-1} \sum_{\{q\}} l(q) \exp(-iqk) \ . \tag{10}$$

Introducing the coordinate $s$ of the $k$th atom along the chain contour, as

$$s = k \cdot l \ , \tag{11}$$

we may first obtain the general vector position $R(s)$ and its derivatives

$$R(s) = R(k) = \sum_{h=1}^{k} l(h) \ , \tag{12a}$$

$$\partial R/\partial s = l^{-1} \partial R/\partial k \simeq l^{-1} \frac{R(k) - R(k-1)}{k-(k-1)} = l^{-1} \cdot l(k) \ , \tag{12b}$$

$$\partial^2 R/\partial s^2 \simeq l^{-2} dl(k)/dk = N^{-1} l^{-2} \sum_{\{q\}} (-iq) \tilde{1}(q) \exp(-iqk) \ , \tag{12c}$$

where the origin of $R$ coincides with the first chain atom.

Let us now define

$$c(k) = N^{-1} \sum_{\{q\}} l(q) \exp(-iqk)/[C(q)l^2]^{1/2} \ , \tag{13}$$

where it is worth pointing out that all the terms in the sum have the same mean-square value, in view of Eq. (9). Now Eq. (8) may be written

$$E = E_0 + \tfrac{3}{2} k_B T \sum_{k=1}^{N} c(k) \cdot c^*(k) \simeq E_0 + \tfrac{3}{2} k_B T \int_0^N c(k) \cdot c^*(k) \, dk \ , \tag{14}$$

as it is easy to obtain from Eqs. (6) and (13), and regarding the index $k$ as a continuous variable. In view of the relationship between $s$ and $k$ [Eq. (11)], we see that a configurational integral along $s$ appears in the above, in analogy with Eq. (1).

Except for the very localized configurational contributions (i.e., $|q| \gtrsim 1$), the function $C(q)$ is well approximated by $a/(1 - b \cos q)$ [see the Appendix in Ref. 8], which in turn may be roughly described by the limiting forms [$(1 - b) \ll 1$]

TABLE I. Parameters $a$ and $b$ for the function $C(q) = a/(1 - b \cos q)$ [see Eq. (15)] applying to polyethylene (PE)[a] and atactic polystyrene (PS).[b]

|     | $a$   | $b$   |
|-----|-------|-------|
| PE  | 0.110 | 0.984 |
| PS  | 0.102 | 0.989 |

[a]Reference 7.      [b]Reference 9.

$$C(q) = \frac{a}{1 - b \cos q}$$

$$\simeq \begin{cases} a/(1-b) & \text{for } 0 \leqslant |q| \leqslant q_{1/2} = (2b^{-1} - 2)^{1/2} \ , \\ \\ 2a/bq^2 & \text{for } q_{1/2} \leqslant |q| \leqslant \bar{q} \ , \end{cases} \tag{15}$$

where $q_{1/2}$ is the half-peak half-width of $C(q)$ while $\bar{q}$ is an upper limit beyond which it roughly tends towards a constant value (contributions with $q > \bar{q}$ may be neglected). Comparison between the above limiting forms and the function $C(q)$ calculated by us for polyethylene (PE)[7] and for polystyrene (PS)[9] is shown in Fig. 1 (see Table I for the parameters). As it may be seen, the greater stiffness of the latter polymer shows up both in a larger peak value $C(0)$ and in a smaller $q_{1/2}$, the product of these two quantities being the same in the two cases. Using Eq. (15), Eq. (13) may be written as

$$c(k) \simeq (Nla^{1/2})^{-1} \left\{ (1-b)^{1/2} \sum_0^{q_{1/2}} \tilde{1}(q) e^{-iqk} \right.$$

$$\left. + (b/2)^{1/2} \sum_{q_{1/2}}^{\bar{q}} |q| \tilde{1}(q) e^{-iqk} \right\} \ , \tag{16}$$

where, for shortness, angular limits instead of integer indices are set to the sums.

Let us now consider the scale $D$ of the experiment, meaning that distances shorter than $D$ cannot be effectively revealed. Since each configurational Fourier component $\tilde{1}(q)$ represents a sinusoidal deformation with a wavelength equal to $n_q = 2\pi/q$ atoms, its limit of observability appears to be naturally associated with the root-mean-square distance $d(q)$ between atoms separated by $n_q$ bonds, i.e.,

$$d(q) = \langle r^2(n_q) \rangle_0^{1/2} \ ;$$

$$\left( \langle r^2(k) \rangle_0 = \frac{l^2}{2\pi} \int_{-\pi}^{\pi} C(q) \frac{\sin^2(qk/2)}{\sin^2(q/2)} dq \right) \quad \text{(Ref. 8)} \ . \tag{17}$$

If we label as $q_D$ the $q$ coordinate for which $d(q) = D$ [Eq. (17)], all the configurational components with $q > q_D$ may be neglected. Consequently, we shall denote as $\bar{1}(k)$, $\bar{R}(s)$, $\bar{c}(k)$, and $\bar{E}$ the "observable" vectors and configurational potential, respectively, obtained from Eqs. (10), (12), (16), and (8) after truncating the sums at $q_D$. Under the same assumption it is easy to see that $E$ reduces to $\bar{E}$ in Eq. (14) if $c(k)$ is replaced by $\bar{c}(k)$. Let us first consider the case of a relatively coarse scale of observation, i.e., $D > D_{1/2}$, where $D_{1/2}$
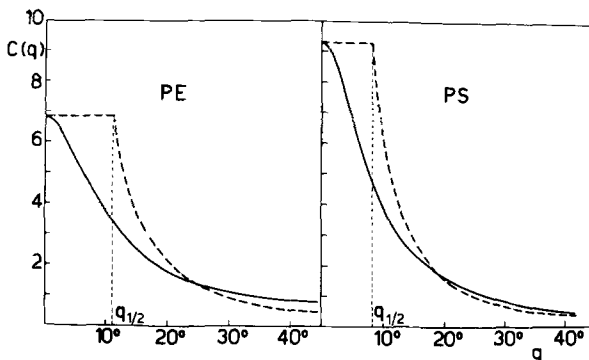
FIG. 1. Plots of the generalized characteristic ratio $C(q)$ calculated for polyethylene (PE) at 127 °C (Ref. 7) and for atactic polystyrene (PS) at 30 °C (Ref. 9) in the rotational state approximation (Ref. 5) (solid lines) and limiting forms of the same function according to Eqs. (15) (dashed lines).

$=d(q_{1/2})$. Consequently, $q_D < q_{1/2}$ and the sum with $q > q_{1/2}$ disappears from Eq. (16), that reduces to [cf. Eq. (10)]

$$\bar{c}(k) \simeq [(1-b)/al^2]^{1/2} \bar{I}(k) \qquad (18)$$

and, in view of Eqs. (11), (12b), and (14),

$$\bar{E} \simeq E_0 + \tfrac{3}{2} k_B T \frac{1-b}{al} \int_0^{Nl} (\partial \bar{R}/\partial s)^2 ds \qquad (D > D_{1/2}) . \qquad (19)$$

The alternative case $D < D_{1/2}$ is best analyzed in the limit $D \ll D_{1/2}$, i.e., $q_D \gg q_{1/2}$, so that we may neglect the first sum in Eq. (16), while starting the second one from $q = 0$. We obtain, substituting $a \cdot a^*$ with $|a|^2$,

$$\sum_{k=1}^{N} |\bar{c}(k)|^2 \simeq \frac{b}{2aN^2 l^2} \sum_{k=1}^{N} \left| \sum_{0}^{q_D} |q| \, \bar{I}(q) \exp(-iqk) \right|^2$$

$$\equiv \frac{b}{2aN^2 l^2} \sum_{k=1}^{N} \left| \sum_{q=0}^{q_D} (-iq) \bar{I}(q) \exp(-iqk) \right|^2 , \qquad (20)$$

and, comparing with Eqs. (11), (12c), and (14),

$$\bar{E} \simeq E_0 + \tfrac{3}{2} k_B T \frac{bl}{2a} \int_0^{Nl} (\partial^2 \bar{R}/\partial s^2)^2 ds \qquad (D \ll D_{1/2}) . \qquad (21)$$

Comparison of Eqs. (19) and (21) with Eqs. (1), apart from an irrelevant additive constant, shows that at large observation lengths $D$ the polymer behaves as an ideal flexible chain while at short $D$ it approaches the stiff (wormlike) model, as qualitatively anticipated at the beginning. In particular, from our calculations on PE[8] and on PS,[9] $D_{1/2}$ is equal to 21 and 29 Å, respectively, while the $q^{-2}$ dependence of $C(q)$ [see Fig. 1 and Eq. (15)] is reasonably well verified at least down to $d(\bar{q}) \approx 8$ Å ($\bar{q}$ is $\sim 3.5 \, q_{1/2}$ for PE and $\sim 4.5 \, q_{1/2}$ for PS). This means that, e.g., the chain dynamics within the wormlike region may only be investigated with quasi-elastic neutron diffraction techniques. At this regard, we remark that the $C(q) \propto q^{-2}$ dependence implies the power law $Q^{8/3} \cdot t_c = \text{const.}$, if $t_c$ is any characteristic time of the dynamic structure factor, $Q$ is the reciprocal coordinate and the free-draining approximation is assumed [see Ref. 8, Eq. (44), $8/3 = \beta = 2/\alpha$]. It is also related with the specific power dependence of the complex modulus $G$ in the high-frequency limit ($G \propto \omega^{1/4}$) as shown by Hearst, Harris, and Beals with a formally different approach.[10] It was also shown by Harris and Hearst for the wormlike chain[1] that the coefficient $K_b$ [see Eq. (1b)] is equal to

$$K_b = 3k_B T/8\lambda , \qquad (22)$$

where $1/2\lambda$ is the chain *persistence length*. By comparison with Eq. (21), we get

$$1/2\lambda = bl/a , \qquad (23)$$

which gives 13.8 and 14.9 Å for PE and PS according to the data of Table I ($l = 1.54$ Å). It should be pointed out that within the same model the mean-square chain length is $\langle r^2 \rangle_0 = L/\lambda = 2Nl^2 b/a$ [in the limit $N \to \infty$, $L = Nl$, see Eq. (42) of Ref. 10, e.g.]. The resulting figures are larger by a factor of about 2.5 than those obtained from the classical relationship $\langle r^2 \rangle_0 = C_\infty Nl^2$, where $C_\infty \equiv C(0) = a/(1-b)$ (cf. Table I). Although the discrepancy is obviously to be attributed to the inadequacy of the wormlike model to represent the real chain, it

is remarkable that an analogous, although smaller, discrepancy may also arise with the ideal model itself, if the flexible range is not properly taken into account (see the following section).

## THE IDEAL WORMLIKE MODEL

The present approach may be easily extended to the ideal Porod–Kratky chain.[4] As it is well known, this model is the limit of a freely rotating chain with $l \to 0$; $\theta$ (bond angle) $= \pi - \tau$, $\tau \to 0$; $l/(1 + \cos\theta) \simeq 2l/\tau^2 = 1/2\lambda$ (persistence length, *finite*); $Nl = L$. Under these conditions, considering that the important values of $q$ are $\ll 1$, Eq. (A10) of Ref. 8 reduces to

$$C(q) = \tau^2/(q^2 + \tau^4/4) ;$$

$$\left[ (2\pi)^{-1} \int_{-\tau}^{+\tau} C(q)\,dq = (2\pi)^{-1} \int_{-\infty}^{+\infty} C(q)\,dq = 1 \right] . \qquad (24)$$

(The square-bracketed identity guarantees that $\langle l^2(k) \rangle = l^2$, the average being over all the skeletal bonds.[8]) The mean-square distance between two chain points separated by a contour length $\Lambda$ is [see Eq. (17) in parentheses, with $k$ (number of intervening bonds) $= \Lambda/l$, $q \ll 1$; using Cauchy's theorem]

$$\langle r^2(\Lambda) \rangle_0 = \frac{l^2}{2\pi} \int_{-\infty}^{+\infty} \frac{\tau^2}{q^2 + \tau^4/4} \cdot \frac{\sin^2(q\Lambda/2l)}{q^2/4} dq$$

$$= \frac{8l^2}{\pi\tau^2} \int_{-\infty}^{+\infty} \left[ \frac{1}{q^2} - \frac{1}{q^2 + \tau^4/4} \right] \sin^2(q\Lambda/2l)\,dq$$

$$= \frac{\Lambda}{\lambda} - \frac{1}{2\lambda^2}(1 - e^{-2\Lambda\lambda}) , \qquad (25)$$

in agreement with a well known result.[2,11] From Eq. (24) we get $q_{1/2} = \tau^2/2$, and, labeling with $\Lambda_{1/2}$ the contour length of the sinusoidal wave with $q = q_{1/2}$,

$$\Lambda_{1/2} = 2\pi l/q_{1/2} = \pi/\lambda , \qquad (26)$$

while the root-mean-square distance between two chain points separated by $\Lambda_{1/2}$ is [see Eqs. (15) and (25)]

$$D_{1/2} = \frac{1}{\lambda}\sqrt{\pi - \tfrac{1}{2}[1 - \exp(-2\pi)]} ,$$

i.e., it is of the same order as the persistence length, as expected. For $D \ll D_{1/2}$, from Eq. (24) we have

$$C(q) \simeq \tau^2/q^2 , \qquad (28)$$

and, after applying the same procedure leading to Eq. (21), the coefficient multiplying the integral is $3k_B T/8\lambda$, in agreement with Harris and Hearst.[1] However, if the mean-square length of the infinite chain were exactly evaluated from the potential of Eq. (21), following Saitô, Takahashi, and Komura (STK),[2] we would obtain $\langle r^2 \rangle_0 = 3L/2\lambda$ instead of $L/\lambda$ [STK may get the correct result only after an *ad hoc* reduction of the above coefficient by a factor 2/3, see Eqs. (2.2), (2.7), and (3.3) of Ref. 2.] Once again, the source of the discrepancy appears to reside in the *approximate* character of Eq. (28), the approximation failing just for $q \to 0$, wherein most of the contribution to $\langle r^2 \rangle_0$ resides. In conclusion, in the limit of infinite chain length, extrapolation of the stiff-chain potential [Eq. (1b)] to obtain $\langle r^2 \rangle_0$ does not appear to be a valid procedure.

## CONCLUDING REMARKS

A quadratic intramolecular potential of average configurations, from which fixed forces may be extracted as canonically conjugated variables [see Eq. (8)], is especially valuable when dealing with problems of molecular dynamics, within the linear approximation for the dynamic equations.[8] In fact, interpretation of such equations as applying to the *average* motion of a canonical system of identical molecules subjected to an ensemble of given external forces, appears to be inevitable. (In this respect, "potential of fixed force" would appear to be a more appropriate definition than the current "potential of mean force.") It should be stressed that the reversal of the interpretation, i.e., considering the potential of Eq. (8) as due to fixed configurations associated with average forces, is incorrect *even within the quadratic approximation*, as clearly demonstrated by Flory [see, e.g., the distribution $W(\mathbf{r})$ given by Eq. (76) (76), Chap. 8 of Ref. 5, and check that the quadratic term in the expansion of $-k_B T \ln W(\mathbf{r})$ is $\neq \frac{3}{2} k_B T r^2 / \langle r^2 \rangle_0$]. On the other hand, in virtually all the equilibrium problems (e.g., scattering from diluted unperturbed macromolecules[12]), the probability distribution applying to the *exact* molecular coordinates is more useful.

In a previous paper by Allegra and Avitabile, a probability end-to-end distribution for polyethylene chains of variable length was derived with the use of the diamond lattice model.[13] Although the resulting distribution $W(\mathbf{r})$ is of the type (average end-to-end distance vs fixed applied force) if truncated at the Gaussian approximation it does not lead to the correct mean-square value $\langle r^2 \rangle_0$; the reason is that attention was deliberately confined to the largest eigenvalue of the intramolecular correlation matrix. The resulting distribution $W(\mathbf{r})$ appears to be reasonably accurate especially for chains with 80 C atoms or more.

It should be pointed out that, in the case of the wormlike chain, Hearst, Harris, and Beals could also distinguish a flexible from a stiff-chain regime by calculating the complex modulus at different frequencies,[10] with the use of a potential containing both components as in Eqs. (1).[1] Also concentrating on the stiff regime with the purpose of investigating the nematic–isotropic transition of rigid chains, Ronca and Yoon proposed an interesting statistical model that bears analogies with the present one [in particular, our quantities $l(k)/l$, $q/l$, $\bar{q}/l$, $\bar{1}(q)$ are analogous to Ronca–Yoon's $t(s)$, $m\pi/L$, $m_c\pi/L$, $2A_m L$].[14]

## APPENDIX

Let us assume that two *fixed*, equal, and opposite forces $\pm \mathbf{f}$ are applied to two given points $P_1$ and $P_2$ of any molecule. Indicating with $\mathbf{r}_f$ the average displacement $P_1 - P_2$, we shall obtain the first coefficient of the series expansion

$$f = A_1 r_f + A_3 r_f^3 + A_5 r_f^5 + \cdots \;, \tag{A1}$$

where $f = |\mathbf{f}|$, $r_f = |\mathbf{r}_f|$. Our starting point will be represented by Eqs. (7) and (10), Chap. 8 of Flory's book,[5] that may be written as

$$Z_t = \int \tilde{Z}_\mathbf{r} \exp(\mathbf{f} \cdot \mathbf{r}/k_B T) d^3\mathbf{r} \;; \tag{A2}$$

$$r_f = k_B T\, \partial \ln Z_t / \partial f \;. \tag{A3}$$

In Eq. (A2), $\tilde{Z}_\mathbf{r}$ stands for the partition function of the molecule under the constraint that the vector distance $P_2 - P_1$ is $\mathbf{r}$. If we integrate over all possible orientations of $\mathbf{r}$, for fixed $r = |\mathbf{r}|$, we get

$$Z_t = \int_0^\infty 4\pi r^2 \tilde{Z}_\mathbf{r} \cdot \sinh(fr/k_B T)/(fr/k_B T)\, dr \;. \tag{A4}$$

Let us introduce the series development

$$\sinh x / x = 1 + \frac{x^2}{3!} + \frac{x^4}{5!} + \cdots \;,$$

and consider that

$$Z = \int_0^\infty 4\pi r^2 \tilde{Z}_\mathbf{r}\, dr \;, \tag{A5}$$

$$\langle r^{2p} \rangle = \int_0^\infty 4\pi r^{2(1+p)} \tilde{Z}_\mathbf{r}\, dr / Z \;, \tag{A6}$$

where $Z$ is the configurational partition function and $p$ is a positive integer. Upon substitution, Eq. (A4) transforms to

$$Z_t = Z\left\{ 1 + \frac{1}{3!}\left(\frac{f}{k_B T}\right)^2 \langle r^2 \rangle + \frac{1}{5!}\left(\frac{f}{k_B T}\right)^4 \langle r^4 \rangle + \cdots \right\} \;. \tag{A7}$$

(Note that the subscript zero is not appended to the averages because the unperturbed state is not required.) Since the vectors $\mathbf{f}$ and $\mathbf{r}_f$ are equally oriented, Eq. (A3) holds for their moduli as well. Using the identity $\partial \ln Z_f / \partial f \equiv (\partial Z_f / \partial f)/Z_f$ and expressing $f$ in the form Eq. (A1), after comparing the coefficients of the resulting polynomial in powers of $r_f$ we get

$$A_1 = 3k_B T / \langle r^2 \rangle \;, \quad A_3 = \frac{3A_1}{2\langle r^2 \rangle} \left(1 - \tfrac{3}{5} K_4\right) \;,$$

$$A_5 = \frac{9}{2} \frac{A_1}{\langle r^2 \rangle^2} \left[\left(1 - \tfrac{3}{5} K_4\right)\left(1 - \tfrac{9}{10} K_4\right) + \tfrac{3}{10}\left(K_4 - \tfrac{3}{7} K_6\right)\right] \cdots \;, \tag{A8}$$

where $K_{2p} = \langle r^{2p} \rangle / \langle r^2 \rangle^p$. For a Gaussian distribution $K_{2p}$ is equal to $[3, 5, 7 \cdots (2p+1)]/3^{p}$[5] and $A_3$ and $A_5$ are bound to vanish, as expected. From Eq. (A1) we may derive the associated potential and the configurational probability $W$,

$$W(\mathbf{r}_f) \propto \exp\left[ -\frac{1}{k_B T}\left(\tfrac{1}{2} A_1 r_f^2 + \tfrac{1}{4} A_3 r_f^4 + \tfrac{1}{6} A_5 r_f^6 + \cdots\right)\right] \;,$$

$$E = -k_B T \ln W \;, \quad f = \partial E / \partial r_f \;. \tag{A9}$$

It should be observed that, even confining ourselves to the Gaussian approximation (i.e., neglecting powers higher than $r_f^2$ within the exponential) from Eq. (A9) we obtain $\langle r_f^2 \rangle = \langle r^2 \rangle$. Conversely, within the same approximation the fixed force $f$ is correctly obtained as $-k_B T\, \partial \ln W / \partial r_f$ [cf. Eq. (A1)].

[1] R. A. Harris and J. E. Hearst, J. Chem. Phys. 44, 2595 (1966).

[2] N. Saitô, K. Takahashi, and Y. Yunoki, J. Phys. Soc. Jpn.

22, 219 (1967).

[3]K. F. Freed, J. Chem. Phys. 54, 1453 (1971).

[4](a) G. Porod, Monatsch. Chem. 80, 251 (1949); (b) O. Kratky and G. Porod, Rec. Trav. Chim. Pays. Bas 68, 1106 (1949).

[5]P. J. Flory, *Statistical Mechanics of Chain Molecules* (Interscience, New York, 1969).

[6]H. Cramer, *Mathematical Methods of Statistics* (Princeton University, Princeton, 1946).

[7]G. Allegra, J. Chem. Phys. 68, 3600 (1978).

[8]G. Allegra and F. Ganazzoli, J. Chem. Phys. 74, 1310 (1981).

[9]G. Allegra, J. Higgins, F. Ganazzoli, E. Lucchelli, and S. Brückner, Macromolecules (submitted).

[10]J. E. Hearst, R. A. Harris, and E. Beals, J. Chem. Phys. 45, 3106 (1966).

[11]J. J. Hermans and R. Ullman, Physica 18, 951 (1952).

[12]D. Y. Yoon and P. J. Flory, Macromolecules 9, 294 (1976).

[13]G. Allegra and G. Avitabile, J. Chem. Phys. 56, 2385 (1972).

[14]G. Ronca and D. Y. Yoon, J. Chem. Phys. 76, 3295 (1982).