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The Multivariate Gaussian Distribution and the Dipole Moments of Perturbed Chains

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ABSTRACT: The behavior of the mean square dipole moment, $\langle\mu^2\rangle$, upon chain expansion was studied several years ago using a multivariate Gaussian distribution. A major conclusion was that $\langle\mu^2\rangle$ would be unaffected by expansion if the chain of infinite degree of polymerization has $\langle\mathbf{r}\cdot\boldsymbol{\mu}\rangle_0 = 0$. Here $\mathbf{r}$ and $\boldsymbol{\mu}$ denote the end-to-end and dipole moment vector, respectively, angle brackets denote the statistical mechanical average, and zero as a subscript denotes the ensemble unperturbed by long-range interactions. This prediction provides the basis for the interpretation of a large body of dipole moment data because many polymers have $\langle\mathbf{r}\cdot\boldsymbol{\mu}\rangle_0 = 0$. Recent simulations, including those reported here, find behavior in conflict with the earlier theory. For some chains with $\langle\mathbf{r}\cdot\boldsymbol{\mu}\rangle_0 = 0$, $\langle\mu^2\rangle$ increases upon chain expansion, and for others it decreases. The earlier theoretical work correctly describes the behavior of those chains for which $\boldsymbol{\mu}_t$ is proportional to $\mathbf{r}_t$, where the subscript denotes a subchain comprised of sufficient bonds so that the distribution of $\mathbf{r}_t$ is Gaussian.

Several years ago the mean square dipole moment, $\langle\mu^2\rangle$, was suggested to be independent of the chain expansion produced by long-range interactions if the resultant dipole moment vector for each repeat unit lies in a plane bisecting the bond angle at a chain atom.[1-3] A first-order perturbation treatment was presented by Nagai and Ishikawa.[4] Following Fixman's application[5] of the multivariate Gaussian distribution[6] for $\mathbf{r}$ and $\mathbf{r}_{ij}$ for the purpose of evaluating α_{r^2}, they employed the multivariate Gaussian distribution for $\boldsymbol{\mu}$ and $\mathbf{r}_{ij}$ to evaluate α_{μ^2}. Here $\mathbf{r}$ and $\boldsymbol{\mu}$ are the end-to-end vector and dipole moment vector for a specified configuration, $\mathbf{r}_{ij}$ is the vector from segment i to segment j in that configuration, $\alpha_{r^2} = \langle r^2\rangle/\langle r^2\rangle_0$, and $\alpha_{\mu^2} = \langle\mu^2\rangle/\langle\mu^2\rangle_0$. Angle brackets denote the statistical mechanical average of the enclosed physical property, and zero as a subscript denotes the ensemble unperturbed by long-range interactions. The result obtained by Nagai and Ishikawa is

$$\alpha_{\mu^2} - 1 = X(\alpha_{r^2} - 1) \tag{1}$$

$$X = \langle\mathbf{r}\cdot\boldsymbol{\mu}\rangle_0^2[\langle r^2\rangle_0\langle\mu^2\rangle_0]^{-1} \tag{2}$$

where X is evaluated for the unperturbed chain of infinite n. Nagai and Ishikawa call attention to two interesting consequences of eq 1 and 2:

A. α_{μ^2} must be one if $\langle\mathbf{r}\cdot\boldsymbol{\mu}\rangle_0$ is zero. Symmetry conditions (symmetry planes, twofold symmetry axes, and symmetry points) that produce $\langle\mathbf{r}\cdot\boldsymbol{\mu}\rangle_0 = 0$ are present in the majority of the polymers of commercial interest. Therefore $\langle\mu^2\rangle$ for such chains should be unaffected by chain expansion. The chains considered by Benoit[1,2] and Stockmayer[3] fall in this category.

B. If a chain has $\langle\mathbf{r}\cdot\boldsymbol{\mu}\rangle_0$ different from zero, it must have $\alpha_{\mu^2} > 1$ if $\alpha_{r^2} > 1$. No chain can have $\alpha_{\mu^2} < 1 < \alpha_{r^2}$ because X cannot be negative.

Soon after the appearance of the article by Nagai and Ishikawa, Doi[7] concluded that eq 1 and 2 are "... valid not only for any order of perturbation but also for any type of interaction...".

It might appear that there is nothing more to be said about the effect of excluded volume on $\langle\mu^2\rangle$ for chain molecules. Some curiousity might be aroused upon reading published accounts of experiments that find $\alpha_{\mu^2} \neq 1$ for certain homopolymers[8-10] and copolymers[11,12] that should have $\alpha_{\mu^2} = 1$ if they were to obey the predictions embodied in eq 1 and 2. Model chains also exhibit curious behavior.[13] A recent study of α_{μ^2} performed by the simulation of model chains perturbed by long-range interactions, finds results in severe conflict with eq 1 and 2 when $\langle\mu^2\rangle$ contains a contribution from an asymmetrically attached side chain:

A′. While it is true that some model chains with $\langle\mathbf{r}\cdot\boldsymbol{\mu}\rangle_0 = 0$ have α_{μ^2} indistinguishable from one, there are other model chains with $\langle\mathbf{r}\cdot\boldsymbol{\mu}\rangle_0 = 0$ and $\alpha_{\mu^2} \neq 1$. The latter chains are in conflict with the conclusion expressed above in A.

B′. A very simple model chain has $\alpha_{\mu^2} < 1 < \alpha_{r^2}$. It exhibits behavior in conflict with the conclusion expressed in B.

Here we report results of additional simulations that demonstrate the conflict with eq 1 and 2 is more general than suggested by the initial simulations. We also identify a heretofore unappreciated assumption in the earlier theoretical work[4,7] that restricts its validity to the case where $\boldsymbol{\mu}$ is proportional to $\mathbf{r}$. Consequently eq 1 and 2 apply only when $X = 1$ (or when $\alpha_{\mu^2} = \alpha_{r^2}$).

Simulations

The previous simulations[13] start with a simple unperturbed rotational isomeric state chain that has the geometry and statistical weights appropriate for unperturbed polyethylene.[14] Excluded volume is introduced via hard-sphere interactions between chain atoms i and $i + h$, with $h < 7$. A dipole moment vector, $\mathbf{m}_i$, was assigned to each bond in the chain. The local coordinate system in which $\mathbf{m}_i$ is simply expressed is depicted in Figure 1. The most interesting chain is the one where every $\mathbf{m}_i$ is $[0\ 0\ 1]^T$ when expressed in the local coordinate system for bond i. Generator matrix calculations then give $\langle\mathbf{r}\cdot\boldsymbol{\mu}\rangle_0 = 0$, but the

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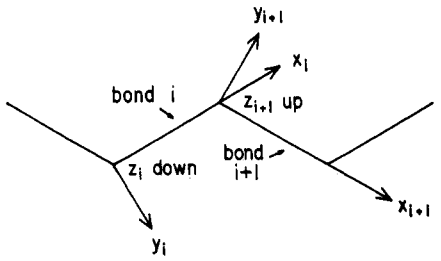

Figure 1. Local coordinate system for $\mathbf{m}_i$ and $\mathbf{l}_i$.

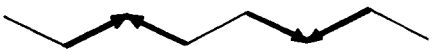

Figure 2. Bond dipole moment vectors in the model chain (n = 7 in the chain pictured).

Table I
Trans Placements and Characteristic Ratios in Unperturbed Chains

		n = 100		n = 202	
σ	P_t	C_r	C_μ	C_r	C_μ
0.43	0.643	7.51 (0)	0.308 (3)	7.81 (10)	0.306 (4)
0.86	0.520	5.80 (2)	0.446 (1)	5.95 (4)	0.445 (1)
1.29	0.447	5.37 (2)	0.506 (1)	5.53 (0)	0.503 (2)

simulation produces $\alpha_\mu^2 < 1 < \alpha_r^2$. This chain stands in conflict with A and B in the introduction. The observation that $\alpha_\mu^2 < 1 < \alpha_r^2$ is easily rationalized because the dipole moment vanishes for fully extended (all trans) subchains that contain an even number of bonds.

The present model considers chains of $3j + 1$ bonds in which

$$\mathbf{m}_i = [0\ 0\ 0]^T \qquad \text{for } i = 1, 4, 7, \ldots, n$$

$$\mathbf{m}_i = [1\ 0\ 0]^T \qquad \text{for } i = 2, 5, 8, \ldots, n-2$$

$$\mathbf{m}_i = -[1\ 0\ 0]^T \qquad \text{for } i = 3, 6, 9, \ldots, n-1$$

The dipole moment pattern, as shown in Figure 2, is that found in poly(oxyethylene) with terminal ethyl groups. Dipole moments vanish for many fully extended subchains, including all fully extended subchains of $6k$ bonds, k = 1, 2, ... Application of the rationalization presented at the end of the preceding paragraph leads to the expectation that the present model chain will have $\alpha_\mu^2 < 1 < \alpha_r^2$. The statistical weight matrix used for each internal bond is

$$\mathbf{U}_i = \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma & \sigma\omega \\ 1 & \sigma\omega & \sigma \end{bmatrix} \tag{3}$$

with several different values of σ. The value of ω was kept constant at 0.034. For each simulation, every internal bond has the same **U**. The remaining details are the same as those in the earlier simulations.[13]

Table I summarizes several properties of the ensembles before introduction of the hard-sphere long-range interactions. The probability for a trans placement decreases, and the chains become more compact, as σ increases. In contrast, the mean square dipole moment becomes larger as σ increases. This result is expected because, as noted in the preceding paragraph, the dipole moment vanishes for fully extended subchains of $6k$ bonds. Dimensionless characteristic ratios formulated from $\langle\mu^2\rangle_0$ are nearly identical for chains of n = 100 and n = 202, but characteristic ratios for $\langle r^2\rangle_0$ are 3–4% larger for the longer chain.

Table II presents the results for two independent simulations for perturbed chains with each σ and n. The hard-sphere size is r^*/l. The number of independent chains in a simulation is 10 000 for n = 100 and 5000 for

Table II
Expansion Factors for Perturbed Chains

		n = 100		n = 202	
σ	r^*/l	α_r^2	α_μ^2	α_r^2	α_μ^2
0.43	2.4	1.197 (1)	0.986 (5)	1.32 (1)	0.97 (2)
	2.7	1.225 (1)	0.976 (2)	1.35 (1)	0.98 (2)
	3.0	1.265 (1)	0.964 (4)	1.42 (3)	0.96 (0)
0.86	2.4	1.307 (8)	0.976 (9)	1.48 (2)	0.96 (2)
	2.7	1.353 (7)	0.968 (5)	1.50 (2)	0.96 (2)
	3.0	1.428 (1)	0.954 (8)	1.60 (7)	0.93 (2)
1.29	2.4	1.360 (3)	0.958 (3)	1.57 (2)	0.95 (0)
	2.7	1.421 (3)	0.943 (2)	1.71 (1)	0.90 (1)
	3.0	1.508 (11)	0.910 (14)	1.76 (12)	0.84 (0)

n = 202. The α_r^2 for the chains with σ = 0.43 are in good agreement with those reported previously.[11] The small differences in α_r^2, which average 0.001 for the shorter chain and 0.02 for the longer chain, can be attributed to the fact that the simulations are necessarily restricted to a finite number of chains. None of the conclusions extracted from Table II would be modified if the α_r^2 were to change by as much as 0.02. The dependence of α_r^2 on the three variables is reasonable; i.e., $(\partial\alpha_r^2/\partial n)_{\sigma,r^*/l}$, $(\partial\alpha_r^2/\partial r^*/l)_{n,\sigma}$, and $(\partial\alpha_r^2/\partial\sigma)_{n,r^*/l}$ are positive. The last derivative is positive because $(\partial\langle r^2\rangle_0/\partial\sigma)_n$ is negative for the range of σ covered.

All of the simulations find $\alpha_\mu^2 < 1 < \alpha_r^2$. The behavior of the dipole moments shows negative values for $(\partial\alpha_\mu^2/\partial n)_{\sigma,r^*/l}$, $(\partial\alpha_\mu^2/\partial r^*/l)_{n,\sigma}$, and $(\partial\alpha_\mu^2/\partial\sigma)_{n,r^*/l}$. These derivatives become positive when α_r^2 replaces α_μ^2. The model chains exhibit behavior in conflict with eq 1 and 2 because $\alpha_\mu^2 < 1 < \alpha_r^2$ and $\alpha_\mu^2 \neq 1$, even though $\langle\mathbf{r}\cdot\boldsymbol{\mu}\rangle_0 = 0$. Clearly behavior incompatible with eq 1 and 2 is not confined to polymers with asymmetrically attached side chains (although the effect is indeed larger in the model chains with asymmetrically attached side chains[13]). It is seen with chains in which each nonzero $\mathbf{m}_i$ lies along the corresponding $\mathbf{l}_i$, and with chains in which the resultant dipole moment vector for a repeat unit lies in the plane bisecting the bond angle at a chain atom. All known model chains with $\alpha_\mu^2 < 1 < \alpha_r^2$ contain subchains for which the dipole moment vanishes upon complete extension.

The simulations are necessarily restricted to chains with finite n. The present and previous[13] simulations show $\alpha_\mu^2/\alpha_r^2 < 1$ when $\langle\mathbf{r}\cdot\boldsymbol{\mu}\rangle_0 = 0$. Furthermore, α_μ^2/α_r^2 becomes smaller as n increases over the range studied. The simulations do not exclude the possible validity of a modified form of eq 1 and 2 which might be written as

$$\lim_{n\to\infty}\left(\frac{\alpha_\mu^2 - 1}{\alpha_r^2 - 1}\right) = \frac{\langle\mathbf{r}\cdot\boldsymbol{\mu}\rangle_0^2}{\langle r^2\rangle_0\langle\mu^2\rangle_0} \tag{4}$$

Equation 4 does not demand $\alpha_\mu^2 = 1$ if $\langle\mathbf{r}\cdot\boldsymbol{\mu}\rangle_0 = 0$. It merely requires that α_μ^2/α_r^2 decrease as n increases.

Reassessment of the Nagai–Ishikawa–Doi Theory

Nagai, Ishikawa, and Doi[4,7] used an extension of the multivariate Gaussian distribution employed by Fixman[5] in his study of α_r^2. The pertinent characterstics of Fixman's application are described with the aid of Figure 3. This figure depicts a chain that is comprised of n_t vectors, denoted by $\mathbf{r}_t$. The $\mathbf{r}_t$ are not identical with bond vectors, $\mathbf{l}_i$. Instead they represent a sequence of bonds (termed a segment) sufficiently large so that the distribution of each $\mathbf{r}_t$ is Gaussian. Using $\mathbf{r}$ to denote the end-to-end distance for the entire chain, we have

$$\mathbf{r} = \sum_{t=1}^{n_t} a_{\mathbf{r},t}\mathbf{r}_t \tag{5}$$

where every $a_{\mathbf{r},t}$ is one for every conceivable configuration.

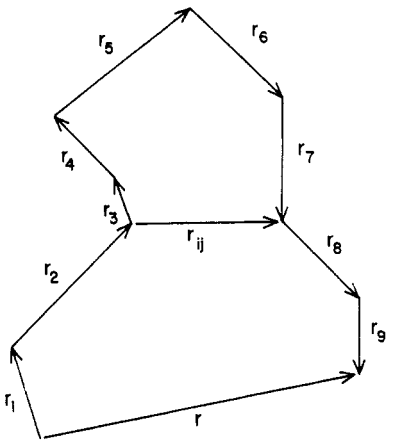

Figure 3. One configuration of a chain comprised of n_t segments with end-to-end vectors $\mathbf{r}_t$, and the chain vector, $\mathbf{r}$. The chain pictured has $n_t = 9$.

The vector from the origin of segment i to the end of segment j is

$$\mathbf{r}_{ij} = \sum_{t=1}^{n_t} a_{\mathbf{r}_{ij},t}\mathbf{r}_t \tag{6}$$

where

$$a_{\mathbf{r}_{ij},t} = 0 \qquad \text{for } 1 \le t < i$$

$$a_{\mathbf{r}_{ij},t} = 1 \qquad \text{for } i \le t \le j \tag{7}$$

$$a_{\mathbf{r}_{ij},t} = 0 \qquad \text{for } j < t < n_t$$

Each $a_{\mathbf{r}_{ij},t}$ has a constant value that applies to every configuration of the chain. Fixman[5] used the multivariate Gaussian distribution to find the simultaneous probabilities, such as $P(\mathbf{r},\mathbf{r}_{ij})$, required for the evaluation of α_{r^2}.

Nagai, Ishikawa, and Doi obtained eq 1 and 2 by an attractive generalization of Fixman's approach. In addition to eq 5–7, they also write

$$\mu = \sum_{t=1}^{n_t} a_{\mathbf{m},t}\mathbf{r}_t \tag{8}$$

and then use the multivariate Gaussian distribution to assess simultaneous probabilities for $\mathbf{r}$, $\mathbf{r}_{ij}$, and μ. But what are the $a_{\mu,t}$ if $\mathbf{r}_t$ must be the end-to-end vector for a *segment* comprised of a number of bonds so large that the distribution of $\mathbf{r}_t$ is Gaussian? If there are segments for which the dipole moment vector vanishes upon full extension, the $a_{\mu,t}$ *cannot be constants that apply to every configuration.* Instead each $a_{\mu,t}$ is a variable that depends on the internal structure of the segment. It must also be able to rotate a vector because μ_t need not be parallel to $\mathbf{r}_t$. Equation 8 is more properly written as

$$\mu = \sum_{t=1}^{n_t} c_{\mu,t}\mathbf{T}_{\mu,t}\mathbf{r}_t \tag{9}$$

where $\mathbf{T}_{\mu,t}$ is a transformation matrix and $c_{\mu,t}$ is a scalar. Neither the scalar nor the transformatio matrix is invariant; they depend on the internal structure of segment t. The multivariate Gaussian distribution is not applicable because it assumes the validity of eq 8, where the $a_{\mu,t}$ are constants.[6]

What problem has been solved if one uses eq 8 and the multivariate Gaussian distribution? Consider a chain in which every *bond* dipole moment vector, $\mathbf{m}_i$, is related to the *bond* vector, $\mathbf{l}_i$, by a nonzero constant.

$$\mathbf{m}_i = (\text{constant})\mathbf{l}_i \tag{10}$$

For this chain, the dipole moment vector for a *segment* (for a collection of consecutive bonds) will be proportional to $\mathbf{r}_t$, and the $a_{\mu,t}$ of eq 8 are indeed constants. The behavior is that predicted by eq 1 and 2, but these two equations can now be written more concisely. Equation 10 demands $\langle \mathbf{r}\cdot\mu\rangle_0^2 = \langle r^2\rangle_0\langle\mu^2\rangle_0$, and therefore, for the case correctly analyzed by Nagai, Ishikawa, and Doi, we obtain $X = 1$ and

$$\alpha_{\mu^2} = \alpha_{r^2} \tag{11}$$

Equations 1 and 2 cannot be used if $\langle \mathbf{r}\cdot\mu\rangle_0 = 0$ because, for such chains, eq 9 must replace eq 8.

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