Comment on: ''Perturbation theory for a polymer chain with excluded volume interaction''

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where $\Delta n(L, t)$ is the time-decaying birefringence for molecules of length L and $P(L)$ is the (normalized) length distribution. Thus, e.g., with a Gaussian distribution,

$$\Delta n(t) = \frac{\int_0^\infty \Delta n_0(L) \exp\left[-\frac{(L-\bar{L})^2}{2\sigma^2}\right] \exp\left[-t/\tau_R(L)\right] dL}{\int_0^\infty \exp\left[-\frac{(L-\bar{L})^2}{2\sigma^2}\right] dL}, \quad (2)$$

where $\Delta n_0(L) = [2\pi(\Delta\alpha')^2 E^2/15nk_BT]^2$, $\Delta\alpha'$ is the anisotropic polarizability per unit length, and all other quantities are defined in Ref. 1. The reader will note that this is *not* equivalent to averaging either the decay time τ_R or the decay rate $1/\tau_R$. Equation (2) implies fast relaxation for short rods and slow relaxation for long rods. Thus, the fit to the long time regime of Figs. 2 and 3 will undoubtedly overestimate the mean length. We have carried out a preliminary numerical analysis of the data using Eq. (2) and find good agreement. A more detailed study is underway. Because of the sensitivity of Eq. (1) to the shape of $P(L)$, we believe the birefringence decay can be developed as an important method for determining $P(L)$.

Schmidt and Wegner argue that highly oriented aggregates with characteristic dimension of 1.3 μm would have a similar decay time. We see no way in which random aggregation of 500–700 macromolecules[5] could lead to a highly oriented particle with dimensions comparable to the length of a single molecule!

Our conclusion is that the field induced birefringence data confirm the rod–coil transition as a single chain phenomenon. The cluster growth and aggregation which occur prior to gelation is the result of the rod-like conformation, but it is not the cause of the conformational change.

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Comment on: "Perturbation theory for a polymer chain with excluded volume interaction"

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Recently, Muthukumar and Nickel[1] published an article entitled "Perturbative theory of a polymer chain with excluded volume." It is a remarkable piece of work, extending at one stroke the three previously known terms of the series, which had taken some 30 years to obtain, to six. In addition they provide a proof that the mean square length $\langle R_N^2(w)\rangle$ is free of terms in $\log N$ to all orders. It is on this proof that we wish to comment. Though it is correct, it raises a small, but important question which deserves clarification.

In the proof, the authors employ a power counting argument to demonstrate that in three dimensions no graph contributing to order $n > 2$ can yield such logarithmic terms. An apparent counterexample is the graph shown in Fig. 1, which, as shown by Barrett and Domb,[2] is a third order graph yielding terms in $\log N$. If the proof is correct, why do Barrett and Domb find logarithms where Muthukumar and Nickel find none? The answer lies in the way the singular part of the propagators is handled. Barrett and Domb have replaced the propagator by a simpler nonsingular function which is asymptotically equal to it. The power counting argument is not valid in this case. On the other hand, Muthukumar and Nickel have simply subtracted propagators so that the singular parts cancel. This step is crucial as is made clear by the following elaboration of the proof:

If a graph contributes to order n, it may be described as having $2n - 3m - 1$ edges and m Θ configurations (Fig. 2): Each edge is represented by a simple propagator of the form

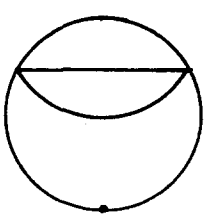

FIG. 1. A third order graph yielding terms in $\log N$.

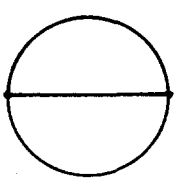

FIG. 2. Θ configuration.

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$$Q_0(q) = \frac{1}{(q^2/6) + E_0}$$

and each Θ by a function:

$$\tilde{\Sigma}_2(q, E_0) - \tilde{\Sigma}_2(0, E_0) = -\pi H_0^2 S(q) ,$$

where

$$S(\sqrt{6E_0}k, E_0) = 4 - \frac{12}{k}\arctan\left(\frac{k}{3}\right) - 2\log\left(1 + \frac{k^2}{9}\right)$$

and h_0 is a scale factor.[2]

These $2(n-m)-1$ factors are subject to integration by $n-2m$ integration "factors" of the form

$$\int \frac{d^3q}{(2\pi)^3} \cdots .$$

Now, following Muthukumar and Nickel, each momentum variable is rescaled:

$$q = q'\sqrt{6E_0} .$$

The simple propagators may be written

$$\frac{1}{E_0(q'^2 + 1)}$$

and

$$\tilde{\Sigma}_2(\sqrt{6E_0}\, q, E_0) - \tilde{\Sigma}_2(0, E_0) = -\pi h_0^2 S(\sqrt{6E_0}\, q) .$$

The result is an integral which is proportional to $E_0^{\frac{1}{2}-n/2}$ for $n > 2$.

I am indebted to Bar-Ilan University and in particular to Professor Cyril Domb for hospitality extended. I am also grateful to Professor Domb for discussion of these and other matters.

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