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Elementary approach to self-assembly and elastic properties of random copolymers

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Abstract

We have mapped the physics of a system of random copolymers onto a time-dependent density functional-type field theory using techniques of functional integration. Time in the theory is merely a label for the location of a given monomer along the extent of a flexible chain. We derive heuristically within this approach a non-local constraint which prevents segments on chains in the system from straying too far from each other, and leads to self-assembly. The structure factor is then computed in a straightforward fashion. The long wave-length limit of the structure factor is used to obtain the elastic modulus of the network. It is shown that there is a surprising competition between the degree of micro-phase separation and the elastic moduli of the system.
I. INTRODUCTION

Co-polymeric systems are of interest because of their promise to provide materials with tailored mechanical properties. In fact de Gennes\textsuperscript{1} has recently proposed the use of self-assembled copolymers to develop artificial muscles. Our own interest in the subject lies in the fact that the random copolymer estane, composed of 75% soft polyester and 25% hard urethane segments, is used as one of the two main components of a binder for high explosives. The binder serves as a shock absorber, rendering the explosive less sensitive to accidental impulses. It is of interest from a safety viewpoint to understand the dependence of its mechanical properties on its average chain length, which may be shortened due to various forms of chemical attack as the high explosive ages over a period of decades.

It has long been part of folklore that the mechanical strength of copolymers arises from a manifestation of self-assembly in the system\textsuperscript{2}. The notion has been that micro-phase separation in random copolymers leads to the formation of a network. Islands of one of the components about the size of tens of Angstroms form its nodes. This network is then said to be the source of the strength of the system. While this is an appealing picture, we are not aware of theoretical or experimental studies which attempt to establish this conclusively. Indeed, we will argue otherwise.

Beginning with the pioneering study of de Gennes\textsuperscript{3}, many theoretical approaches have been developed to study self-assembly in copolymers, both diblock and random\textsuperscript{4-8}. While de Gennes' original paper was clear in its concept, the formalisms that followed, including our own version\textsuperscript{8}, are weighted in our opinion by important details which obfuscate the origin of self-assembly. de Genne's idea was that while the two species in the system have a natural propensity for phase separation on a macro-scale, the fact that there is covalent bonding between the species along the chains prevents this from occurring. de Gennes modeled this effect via a mechanical constraint which costs the system energy if the species stray too far from each other. Later formalisms tried to derive this constraint using sophisticated methods. These models have generated much interest in novel ordered phases of the system\textsuperscript{9,10}. 

\textsuperscript{2}
Some of these models derive a structure factor $\hat{S}(k)$ which becomes zero in the long wavelength limit $k = 0$. We know from Kirkwood's work$^{11}$ that $\hat{S}(k = 0)$ is proportional to the elastic moduli of the system. Thus in essence these models are unable to address the mechanical properties of the system. However, there are notable exceptions$^{12,13}$. Yeung et al$^{13}$ obtained expressions for the bulk modulus and the bending modulus from the structure factor. Our paper provides an alternative method for analyzing the mechanical response of micro-phase separated segmented copolymer systems to infinitesimal strains.

We use a density functional formalism to first derive in a heuristic manner a model for self-assembly in segmented copolymers, and then argue that there is in fact a competition between the degree of microphase separation and the mechanical properties of the system. The model utilized is phenomenological, and it is hoped that our paper will stimulate future studies to make the technique more rigorous using more realistic interaction models. The main justification for such an approach lies in the fact that the theory yields results concerning self-assembly and elastic moduli which can be compared successfully with experimental data.

Perhaps the simplest way to show that the network formed by self-assembly in copolymers is not the dominant factor in determining their mechanical properties is to note that the typical distance between the the domains is $\ell \sim 100 \text{\AA}$. Consequently, the contribution to the modulus from the self-assembled network may be approximated by the following expression for the energy density, viz., $kT/\ell^3$, where $k$ is Boltzmann's constant, and $T$ is the absolute temperature. At room temperature, when $kT \sim 0.03eV$, we get a modulus $\sim 3 \times 10^4 \text{dynes/cm}^{-2}$, which is two orders of magnitude less than the measured value. Thus the effective $\ell$, which determines the mechanical modulus of the system must be much smaller than 100\text{\AA}. In other words, it is the physics which occurs on a length scale much smaller than the inter-aggregate distance which determines the mechanical modulus of the system. The rest of the paper can be viewed as a formalization of this physical reasoning.

We have tried to achieve a level of presentation which lies between de Gennes' original
plan and the later ideas of self-assembly. The motivation for the paper arose from an interest in a specific copolymer, viz., estane, and all the numerical estimates for various quantities in the paper were made for this system. But the theory we present here is applicable more generally. Furthermore, along the way, we also provide evidence that the system exhibits a transition to a state analogous to the entangled state for homopolymers as the chain length is increased.

II. DENSITY FUNCTIONAL FORMALISM

We shall begin with an approach developed by us in an earlier paper. We shall state only the main results briefly below.

The propagator for a single flexible chain may be represented by from methods in functional integration that:

$$\langle 1, n | \left[ \partial_n - \left( \frac{b^2}{6} \right) \nabla^2 \right]^{-1} | 2, 0 \rangle \sim \int D^2 \psi \psi^*(\vec{R}_1, n) \psi(\vec{R}_2, 0) \exp\left[ -\beta F_0 \right]$$

$$\beta F_0 = \int dn'd^3x \psi^*(\vec{x}, n') \left[ \partial_{n'} - \left( \frac{b^2}{6} \right) \nabla^2 \right] \psi(\vec{x}, n')$$

where $D^2 \psi = D\psi^* D\psi$, $\beta = \frac{1}{k_B T}$, $k_B$ is Boltzmann's constant and $T$ is the temperature. Thus we have a way of thinking about a system of flexible polymers, in terms of $\psi(\vec{x}, n)$ and an energy functional $\beta F_0$ which is isomorphic to one that describes diffusion. Here $(\vec{x}, n)$ labels the location $\vec{x}$ in physical space, of the $n$-th segment of a chain. This method is equivalent to the Edwards representation in terms of a Feynman path integral. The new method is a compact notation to describe many independent chains beginning with the partition function $Z = \int D^2 \psi \exp\left[ -[\beta F_0] \right]$. The main advantage of the functional path integral formalism is that one can model more easily interactions in systems with large numbers of polymers by adding an interaction term as shown by the following example:

$$\beta F_0 \rightarrow \beta F = \beta F_0 + \beta \Delta F$$

$$\beta \Delta F = \int d^3xdn \left( V(\psi(\vec{x}, n), \psi^*(\vec{x}, n)) \right)$$
where \( V(\psi, \psi^*) \) represents the interaction between segments.

Following the convention in quantum field theory, \( |\psi(\vec{x}, n)|^2 \) is interpreted as the probability of finding a polymer segment at a given location in space.

Kleinert\(^\text{20}\) has proposed a similar formalism for homopolymer melts. Ferrari and Lazzizzera\(^\text{21}\) have provided yet another way of investigating two entangled polymer rings. However, this paper uses the new formalism to probe the physics of many copolymers in a broader sense.

We will now generalize Eqn. (1) to describe random copolymers. Let us suppose for the moment that the monomer lengths of the two types of monomers in the system are the same. We propose to generalize Eqn. (1) by allowing \( \psi \) to take on two possible values which represent the probability amplitude that either \( A \) or \( B \) type of monomer is present at a given location along a chain in the system. This can be achieved by going from a scalar to a pseudo-spin notation:

\[
\psi(\vec{r}, n) \rightarrow \Psi(\vec{r}, n) \equiv \begin{pmatrix} \psi_A(\vec{r}, n) \\ \psi_B(\vec{r}, n) \end{pmatrix}
\]

(3)

The original energy functional \( \beta \mathcal{F}_0 \) is transformed as follows:

\[
\beta \mathcal{F}_0 \rightarrow \int d^3x dn \, \beta \mathcal{F} = \int d^3x dn \, \Psi^\dagger(\vec{x}, n) \left[ \partial_n \left( \frac{b^2}{6} \right) \nabla^2 \right] \Psi(\vec{x}, n)
\]

(4)

The notation in this classical model is reminiscent of that in Pauli’s generalization of the Schrödinger equation to describe particles with spin 1/2. Note that Eqn. (4) describes the entropy of the system\(^\text{17}\). The model is qualitatively similar to that of Wu et al\(^\text{18}\) who used an Ising-like lattice model with long-range interactions to describe oil-water-surfactant mixtures.

Excluded volume interactions could be accounted for by an interaction term of the following sort:

\[
\beta \mathcal{F}_{\text{interact}} = \left( \frac{\beta}{2} \right) \int d^3x dn' \, (|\psi_A(\vec{x}, n)|^2 |\psi_B(\vec{x}, n')|^2) \begin{pmatrix} \epsilon_{AA} & \epsilon_{AB} \\ \epsilon_{AB} & \epsilon_{BB} \end{pmatrix} (|\psi_A(\vec{x}, n')|^2 |\psi_B(\vec{x}, n')|^2)
\]

(5)
Note that upon instituting incompressibility at each spatial point, the matrix interaction term reduces to a scalar interaction term whose coefficient is \( \frac{1}{2} \beta (\epsilon_{AA} + \epsilon_{BB} - 2\epsilon_{AB}) \equiv \chi/2 \) where \( \epsilon_{AB} \), and \( \epsilon_{AA} \), \( \epsilon_{BB} \) are the inter-phase, and intra-phase interaction energies respectively. Such an excluded volume term alone is insufficient to describe self-assembly, as argued originally by de Gennes\(^3\).

The approach used in this paper will be a simple method to obtain the long-range mechanical constraint first derived by de Gennes\(^3\) in a phenomenological manner. Towards that end, we shall use polar decomposition, viz.,

\[
\psi_A(\vec{r}, n) = \sqrt{c_A(\vec{r}, n)} \exp(i\phi_A(\vec{r}, n)) \\
\psi_B(\vec{r}, n) = \sqrt{c_B(\vec{r}, n)} \exp(i\phi_B(\vec{r}, n))
\]

Let us also introduce the following notation:

\[
C(\vec{r}, n) \equiv \begin{pmatrix} c_A(\vec{r}, n) \\ c_B(\vec{r}, n) \end{pmatrix} \\
\Phi(\vec{r}, n) \equiv \begin{pmatrix} \phi_A(\vec{r}, n) \\ \phi_B(\vec{r}, n) \end{pmatrix}
\]

(6)

where \( c_A, c_B \) represent the local normalized concentrations of the two species in the system.

Eqn.(4) can now be written approximately as:

\[
\beta f(C(\vec{r}, n), \Phi(\vec{r}, n)) \approx \\
- i\Phi^t(\vec{r}, n) \vec{\partial}_n C(\vec{r}, n) - \left( \frac{i^2}{6} \right) \left[ \frac{1}{4} C^t(\vec{r}, n) \vec{\nabla}^2 C(\vec{r}, n) + \Phi^t(\vec{r}, n) \vec{\nabla}^2 \Phi(\vec{r}, n) \right]
\]

(8)

where we have ignored terms which can be written as derivatives, employed integration by parts, only retained terms quadratic in the concentration, normalized concentrations by the average number density \( c_0 \) of chains, and normalized all lengths by \( c_0^{1/3} \).

Furthermore we shall express the local normalized concentrations as:

\[
c_A(\vec{r}, n) = 1 + c(\vec{r}, n) \\
c_B(\vec{r}, n) = 1 - c(\vec{r}, n)
\]

(9)
with this the model can be written as:

\[
\beta \mathbf{f} (c(\vec{r}, n), \Phi(\vec{r}, n)) \approx \beta \mathbf{f} - \left( b^2 \frac{1}{6} \right) \left[ \Phi^t(\vec{r}, n) \nabla^2 \Phi(\vec{r}, n) + \frac{1}{2} c(\vec{r}, n) \nabla^2 c(\vec{r}, n) \right]
\]  

where \( J^t = (1, -1) \).

The physical idea we wish to describe is that in this system of averaged chains, different segments of the same chain or different chains come together and form spatially coherent aggregates, which in turn are arranged a mean distance \( \ell \) apart. The final goal is to obtain the structure factor of a random copolymer which displays self-assembly.

We will now allow the two species in the system to interact through a simple interaction term. This model allows the two species in the model to interact through the phases of the two fields \( \psi_A \) and \( \psi_B \). The model can be thought of as allowing the phases of the two species to fluctuate randomly, subject only to a single constraint. The constraint is imposed on the system through the use of a Lagrange multiplier. Thus the interaction term can be termed a Random Phase Approximation (RPA). We shall shortly compare the results of the current model to those obtained using the more conventional RPA\(^4\). The minimal model we employ is:

\[
\beta \mathbf{f} \rightarrow \beta \mathbf{f} + \beta \Delta \mathbf{f}
\]

\[
\beta \Delta \mathbf{f} = \left( \frac{1}{2} \right) \Phi^t(\vec{r}, n) \mathbf{W} \Phi(\vec{r}, n)
\]

\[
\mathbf{W} = \nu \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}
\]

where \( \nu \) is a Lagrange multiplier, and as will be shown later:

\[
\nu^{-1} \propto \chi = \beta (\epsilon_{AA} + \epsilon_{BB} - 2\epsilon_{AB})
\]

Here \( \chi \) is the Flory-Huggins separation constant, and \( \epsilon_{AB} \), and \( \epsilon_{jj} \) \((\forall j = A, B)\) are the inter-phase, and intra-phase interaction energies respectively. The off-diagonal elements of the matrix \( \mathbf{W} \) permit a coupling between the species. The results regarding self-assembly in
copolymers which follow will be compared successfully with experiments in section III. We will also discuss there some of the shortcomings of this model.

Mathematically, the motivation for the model comes from observing that a Gaussian functional integration is given by \( \int \mathcal{D}\Phi \exp(-G^{-1}\Phi^2 - J\Phi) \sim \exp(J^2G/4) \), where \( G \sim \) structure factor. It will turn out that with the choice of interaction term we have made, \( G^{-1} \rightarrow \text{constant} \) as \( k \rightarrow 0 \). This enables us to address the elastic properties of the system.

The \( \Phi \) (Gaussian) functional integration in the partition function can be performed, and the result can be expressed in Fourier space:

\[
Z \sim \int \mathcal{D}\hat{c} \exp \left[ -\frac{1}{2} \int \frac{d^3k}{(2\pi)^3} \int \frac{d\omega}{2\pi} \hat{c}^*(k,\omega) \hat{S}^{-1}(k,\omega) \hat{c}(k,\omega) \right]
\]

\[
\hat{S}(k,\omega) = \left[ \frac{b^2k^2}{6} + \hat{V}_{SA}(k,\omega) \right]^{-1}
\]

\[
\hat{V}_{SA}(k,\omega) = -J^t \frac{\omega^2}{(\mathbf{W} + b^2k^2/3)} J
\]

where \( \hat{c} \) is the Fourier transform of \( c \), and \( \hat{S}(k,\omega) \) is the structure factor. The terms containing \( \omega \) come from the \( \partial/\partial n \) operator in the original energy functional, and we shall henceforth identify \( \omega \) with \( 1/N \), \( N \) being the average chain length in the system. This interpretation is analogous to identifying a wavenumber \( k \) with a characteristic length scale \( d \) via \( k = 2\pi/d \).

The second term in the denominator of \( \hat{S}(k,N) \) viz., \( \hat{V}_{SA} \) is the Fourier transform of a screened Coulomb-like interaction. In real space, this term will appear as a screened interaction term \( V_{SA}(r) \sim \exp(-r/\lambda)/r \), with \( \lambda \sim b/\sqrt{\nu} \). In this way we have obtained as advertised a nonlocal constraint. Self-assembly arises due to the competition between the Flory Huggins term which promotes phase separation on a macroscale, and \( V_{SA} \) which prevents \( A - B \) segments from straying too far from each other.

The generic form of \( \hat{V}_{SA} \) is similar to other models in the literature that are used to study self-assembly. We have invoked a heuristic derivation of the nonlocal constraint which leads to self-assembly, and our \( V_{SA}(r,N) \) can be compared in detail to previous theories. The main difference is that we have a screened interaction, while the theories of de Gennes and Leibler had a long range (\( \sim 1/r \)) interaction. This causes \( \hat{S}(k = 0) \) in their theories
to vanish, along with the elastic modulus\textsuperscript{11}. de Genne’s original derivation of self-assembly invoked an analogy with electrostatic interactions in dielectric media\textsuperscript{3}. In fact, one can make a connection to his formulation by formally setting $W \rightarrow 0$ in Eqn. (13), which leads to a coefficient of $k^{-2}$ in the denominator of $\hat{S}(k)$ which is proportional to $(Nb)^{-2}$. This coefficient may be compared to $\sim (nb)^{-2}$ that was obtained by de Gennes, where $n$ was interpreted by him as the average number of monomers between cross-links. Leibler\textsuperscript{4} later showed that $n$ should be replaced by $N$, the total chain length, so that his coefficient is proportional to $(Nb)^{-2}$, in agreement with experiments that followed, and with our theory.

Our model will be shown to lead to nontrivial results such as the dependence of the peak location ($k^*$) of the structure factor on the chain length $N$. We obtain $k^* \sim N^{-1}$, in agreement with experiments. Other models lead to similar results, but are much more involved. This example is offered as evidence of the validity of our phenomenological model. Further successful comparisons with experiment are offered in the next section.

\section*{III. SELF-ASSEMBLY AND THE ELASTIC MODULUS}

Upon expanding the denominator of $\hat{S}(k, \omega)$ (Eqn. (13)) in powers of $k$, we obtain to $O(k^4)$:

\begin{align}
\hat{S}(k, N) &\approx \frac{1}{2\nu^{-1}N^{-2} - \xi(\nu, N, b)k^2 + \Lambda(\nu, N, b)k^4} \\
\xi(\nu, N, b) &\approx \frac{(b^2/6)(4\nu^{-2}N^{-2} - 1)}{2b^4\nu^{-3}(3N)^{-2}}^{1/4} \\
\Lambda(\nu, N, b) &\approx \left(2b^4\nu^{-3}(3N)^{-2}\right)^{1/4}
\end{align}

In order to facilitate an identification of the parameter $\nu$, we first note the obvious identity:

\begin{align}
\mathcal{F}[c] &= \int \frac{d^3k}{(2\pi)^3} \frac{d\omega}{2\pi} \hat{f}(k, \omega) \\
&= \frac{1}{2} \int \frac{d^3k}{(2\pi)^3} \frac{d\omega}{2\pi} \hat{c}^*(k, \omega) \hat{S}^{-1}(k, \omega) \hat{c}(k, \omega)
\end{align}

Furthermore, from general considerations, for $k = 0$, the energy density must have the following generic form related to the Flory-Huggins approach:
\[ i(k = 0, \omega) = \frac{1}{2} \hat{c}^*(k = 0, \omega) \chi \hat{c}(k = 0, \omega) \tag{16} \]

Therefore from Eqns. (14, 15, 16) we immediately make the following identification:

\[ 2\nu^{-1}N^{-2} = \chi \tag{17} \]

where \( \chi \) is the Flory-Huggins separation parameter (see Eqn. (12) for the form of \( \chi \) for a copolymer). Consequently:

\[
\hat{S}(k, N, \chi, b) \approx \frac{1}{\chi - \xi(\chi, N, b)k^2 + \Lambda^4(\chi, N, b)k^4} \\
\xi(\chi, N, b) = \left( \frac{b^2}{3} \right) [(\chi N)^2 - 1] \\
\Lambda(\chi, N, b) = 6^{-1/2}N\chi^{3/4} \tag{18}
\]

**Self-assembly:**

It is seen that there will be micro-phase separation when \( \chi N > 1 \). Beyond this critical value, \( \xi > 0 \), so that there is a peak in the structure factor. Thus the onset of self-assembly is defined by \( \chi N = 1 \). As such the onset of self-assembly is a Lifshitz point, where the coefficient of the gradient smoothing term vanishes, but the structure factor remains finite. In this sense the onset of micro-phase separation is a continuous transition. This is in contrast to the Order-Disorder transition (ODT), which is a discontinuous, first-order phase transition, and described theoretically by a singularity in the structure factor. Leibler was the first to discuss the difference between the ODT and the onset of the micro-phase transition. In an earlier paper, we used Renormalization Group techniques to show that the onset of self-assembly is indeed a Lifshitz point, in agreement with the experimental results of Koberstein et al. The shortcoming of the current model is that while we obtain rather easily the dependence of of various quantities on the chain length \( N \), it tacitly assumes that the random copolymer system is already in a composition range where self-assembly is possible, as shown by the indedependence of the self-assembly criterion on the average number fraction of the species in any given chain. A higher order theory will recover this dependence, as shown by Leibler. Since our main concern is to understand the dependence of the elastic
moduli on the chain length of estane or similar elastomers, whose composition is such that self-assembly is guaranteed, the present theory is sufficient.

The asymptotic $k^{-4}$ dependence is consistent with Porod's law. Conventionally, the location of the peak indicates the mean inverse distance between the self-assembled aggregates, while the width is interpreted as a measure of the deviation from this mean. Our estimate of the critical value of $\chi N$ is of course different from the estimate of its critical value ($\sim 10$) for the Order-disorder transition (ODT)\textsuperscript{4}. The parameter $\chi$ will change with the system being considered. It also possesses a temperature dependence\textsuperscript{17}. Typical values of $\chi$ used in the literature are $O(10^{-2})$\textsuperscript{6}.

We will now present some numerical results for the particular case of estane. But the conclusions we draw from them are more general. Now the basic model we are using is that of a flexible chain, such that the monomer is linear and rigid, and is connected freely at either end to other segments. In the case of estane, a random copolymer, things are a bit more complicated, where the monomer lengths are unequal. We used an average value of the monomer length $b \rightarrow \bar{b} = f_A b_A + f_B b_B$, where $A, B$ are labels for the two components in the system, and $f_A, f_B = 1 - f_A$ are the relative average number fractions of the two species. In other words, if the average chain length is $N$, with $N = N_A + N_B$, $N_A, N_B$ being the average number of monomers of types $A$ and $B$ respectively, then $f_A = N_A/N$, $f_B = N_B/N = 1 - f_A$.

Sewell\textsuperscript{25} has performed Molecular Dynamics (MD) simulations on a single chain composed of the relatively hard, chevron-shaped\textsuperscript{24} urethane monomers and soft ester segments connected by a butanediol group. He finds at room temperature that due to transformations between cis and trans conformations and also due to partially folded configurations, the average length of the hard and soft monomers as well as the butanediol group fluctuates. From these simulations it turned out that the average monomer length of estane $\bar{b} \approx 8\text{Å}$. The bond fluctuations we just discussed occur on a time scale of femtoseconds, so that on the time scales (equilibrium) that we are interested in, the monomer length is in effect constant. The second and final parameter is the Flory-Huggins separation parameter $\chi$. We will follow literature in restricting its magnitude to be $O(10^{-2})$. Adjustments were made to $\chi$ to obtain
agreement with the location of the peak in the structure factor (at $\sim 0.018\text{\AA}^{-1}$) for estane$^2$. The paper by Bonart et al$^2$ appears to be the first paper, at least on estane, to provide experimental evidence for self-assembly through the measurement of the structure factor using small angle X-ray scattering (SAXS). For completeness, we note that using a higher value for $b$ leads to a peak at a lower wavenumber, and conversely, a lower value for $b$ yields a peak at a higher wavenumber. As a concrete example, $b = 4\text{\AA}$ gives a peak at about $0.03\text{\AA}^{-1}$. The peak in the theoretical structure factor appears to be quite sensitive to the value of $b$.

The location of the peak also depends on the chain length$^6$. We have plotted in Fig.(1) the structure factor using parameters representative of estane viz., $b = 8\text{\AA}$, $\chi = 0.02$, to depict this for $N \sim 10^3$. The peak is seen to shift towards larger wavenumbers as $N$ decreases.

On the other hand, near the critical chain length $N_c$ below which self-assembly does not take place ($\chi N_c < 1$), we find a rather different behavior, as depicted in Figs.(2). Between chain lengths of 80 and 100, the peak is seen to shift in Fig.(2) as before, but between 75 and 80, the peak actually shifts the other way, towards lower wavenumbers, as the chain length is decreased. For the parameters chosen, $N_c = 50$. Note that $k^* \sim 0.015\text{\AA}^{-1}$ for $N = 100$, in reasonable agreement with the experiments of Bonart$^2$. The anomalous behavior which occurs near the onset of self-assembly (as the chain length is varied) can be understood in the following way. Below $N < N_c$, there is no self-assembly, and the peak in the structure factor occurs at zero wave-number. As $N$ is increased just past $N_c$, $k^*$ attains a non-zero value, and it continues to increase as the aggregates begin to locate a finite distance from each other. But for very large values of $N >> N_c$, the likelihood of finding self-assembled aggregates near each other goes down, due to physical constraints on the motion of these aggregates through a thicket of long polymers. In addition, as the chain length increases, the number of aggregates also increases, thereby forming a network with permanent junctions, which further reduces the mobility of the aggregates. Thus we should expect $k^*$ to decrease
for $N >> N_c$. This behavior is depicted pictorially in Fig.(3).

For $N >> N_c$, our theory yields

$$k^* = 6^{1/2} \chi^{-1/2} (N \bar{\rho})^{-1} + \mathcal{O}(N^{-2})$$  \hspace{1cm} (19)

which is in reasonable agreement with the experiments of Almdal et al\textsuperscript{26}, who obtained an exponent of $N$ closer to 0.8 for a diblock system composed of poly(ethylene-propylene)-poly(ethyl-ethylene) (PEP-PEE).

The transition in the behavior of $k^*$ as a function of increasing $N$ is analogous to the entanglement transition in homopolymer melts. In the present case, there is a restriction on the motion of the self-assembled aggregates beyond the transition. It is possible that earlier experiments such as those of Almdal et al\textsuperscript{26} missed this transition because they worked with chain lengths $N > N_c$ for the PEP-PEE system. The lowest value of $N$ they used was $\sim 120$, which is above $N_c \sim 30$ we obtain from our theory for their system.

Part of the motivation for investigating this aspect of the behavior of random copolymers came from simulation results with a Bond Fluctuation Model (BFM) performed by Sewell\textsuperscript{25}. He found for short chain systems, a dependence of $k^*$ on $N$ similar to that obtained from our theory below the transition just discussed. And this appeared to be in contradiction with experimental results, such as those of Almdal et al, which as we have argued, pertain to the long chain regime. There is also evidence in Sewell's results of the beginning of a roll-over of the peak location as the chain length is increased. Limitations on hardware prevent these simulations from being carried out for longer chains. New experiments will be required to confirm this idea.

Figure (4) displays the peak height (maximum) of the structure factor as the chain length is increased. It becomes apparent then that the onset of self-assembly is signaled by a minimum in the fluctuations, caused by the formation of nanoscale aggregates. The maximum in the fluctuations is approached asymptotically. The asymptotic behavior of our theory is similar to previous ones. Now a minimum in the free energy is usually interpreted as the ODT\textsuperscript{6}. The free energy density is proportional to the inverse of the structure factor at the
quadratic level where we are working, since higher order correlations were neglected in favor of simplicity. As such the approximations used thus far yield an ODT only asymptotically. It may be tempting to argue that the ODT occurs when the peak value of the structure factor turns the corner, so to speak, in Fig.(4). But one needs more information, such as from Leibler's theory to say precisely when this occurs. One would have to start with Eqn.(8) and retain cubic and quartic terms in the concentration $c(\vec{r},n)$ in order to treat the ODT correctly. But our main interest is in polymers like estane with $\chi N \sim 1 << (\chi N)_{ODT} \sim 10$, and their associated mechanical properties.

- **Mechanical properties:**

From previous work\textsuperscript{11,27}, we know that Young's modulus $Y$ is given by the long wavelength limit of the structure factor:

$$Y = 2c_0\beta^{-1}\chi^{-1} = 2\beta^{-1}c_{\text{effective}}$$  \hspace{1cm} (20)

where $c_{\text{effective}}$ is interpreted as the chain density between cross-links. Now, the larger the value of $\chi$, the greater the degree of microphase separation, in the sense that $\xi$ increases with $\chi$, making the peak in the structure factor more pronounced. On the other hand, from Eqn.(20) we see that an increasing $\chi$ implies a lower elastic modulus. In this sense there is competition between microphase separation in the system and its mechanical properties. In fact, it is easy to see that for a sufficiently low value of $\chi$, when $\xi < 0$, there will be no micro-phase separation, and yet the value of $Y$ increases.

Physically what this means is that the strength of the copolymer network comes from either entanglement or possibly physical cross-linking (hydrogen bonding or Van der Waal's interaction), which occurs in the interstitial region between the nanoscale aggregates which signal self-assembly. It can be seen intuitively that the lower the value of phase separation parameter $\chi$, the greater the possibility that the polymeric strands will enmesh with each other.

At room temperature we obtain $Y \sim 200 \text{ bars}$ for estane. The mechanical experiments to determine elastic moduli of polymeric samples are notoriously difficult to conduct, and
usually have large errors associated with them. And the value for Young’s modulus we obtained is in order-of-magnitude agreement with measured values for estane\textsuperscript{28}. Another reason for the disagreement could be that the samples of estane used in the mechanical experiments may not be identical to the ones used by Bonart.

We have obtained an expression for $Y$ which depends on the chain length $N$ solely through the chain density $c_0$. It is therefore suggestive that as chain length degradation occurs, the Young’s modulus will drop precipitously. However, in estane, it so happens that in the interstitial region between the nanoscale aggregates, there is physical cross-linking which occurs between hard segments of urethane\textsuperscript{24} which help make up the chain. This happens because not all the hard segments segregate into nanoscale domains, as will be shown in the next section. Thus, even though a chemical attack such as hydrolysis might scission the chains, the effective $c_0$ changes but little until the sample is eventually liquefied. This is because a cut in a given chain is isolated between successive physical links. Indeed, Young’s modulus of estane remains essentially unchanged in experiments\textsuperscript{28} as $N$ is cut down from 100 to about 50. Note as the temperature $T$ rises, we expect $\chi = a - b/T$ ($a, b$ are constants) to increase, thereby lowering the modulus and enhancing domain growth. This is consistent with the preliminary experimental data currently available\textsuperscript{28}.

We will now briefly compare our results for elastic moduli, which we have done in a manner consistent with the ideas of Kirkwood\textsuperscript{11}, with the approach of Yeung et al\textsuperscript{12}. These authors use a long wavelength expansion of their structure factor near the Bragg peak for a microphase separated diblock copolymer viz., $\tilde{S}(k) \sim (Bk^2 + Kk^4)^{-1}$. $B$ is identified with the bulk modulus and $K$ with the bending modulus. They considered ordered phases of self-assembly in copolymers when lamellar structures extend through the extent of the material. In this paper, the interest is in segmented copolymers which exhibit a disordered phase or self-assembled aggregates. Yeung et al presented results for the bending modulus $K$ as a function of $\chi$ and $N$. It shows $K$ increasing with $\chi N$. No comparison with experiments was provided, presumably because data were unavailable. Their result is consistent with the $K \equiv \Lambda^4$ obtained in this paper. In spite of this, our approach at first glance may seem
inconsistent with Yeung et al, in that we explicitly use the $k = 0$ limit of the structure factor to obtain the elastic moduli. The resolution of this paradox lies in the fact that while Yeung et al used a long wavelength expansion, they nonetheless use a more local approach than ours by studying the mechanical response of the system at a length scale of $\sim \mathcal{O}(\bar{b})$. We have considered the response of the system in the thermodynamic limit, viz., $k = 0$. The moduli calculated in this paper are consistent with the limited experimental results available to us for estane.

IV. MORPHOLOGY OF THE SELF-ASSEMBLED DOMAINS

As shown earlier, self-assembly can be described by an effective energy functional given by:

$$\beta \mathcal{F}[c] = \left(\frac{1}{2}\right) \int \frac{d^3k}{(2\pi)^3} \frac{d\omega}{2\pi} \hat{c}^*(k, \omega) \hat{S}^{-1}(k, \omega) \hat{c}(k, \omega)$$  \hspace{1cm} (21)

By extremizing this functional with respect to $\hat{c}^*$, we obtain a partial differential equation whose solutions describe the morphology of the domains which are formed in self-assembling random copolymers.

$$\left[\chi + \xi(\chi, N, \bar{b}) \nabla^2 + \Lambda^4(\chi, N, \bar{b}) \nabla^4 \right] c(\vec{r}, N) = 0$$  \hspace{1cm} (22)

The equation is linear and can be easily solved in various geometries. Since our own interest is in estane whose composition is such that the domains are expected to be spherical blobs on the average, we look for solutions of the form $c(\vec{r}) \sim \exp(ipr)/r$. This yields a condition on $p$:

$$\chi - \xi(\chi, N, \bar{b}) p^2 + \Lambda^4(\chi, N, \bar{b}) p^4 = 0$$

$$p^2 \approx \left(\frac{3}{\chi(N\bar{b})^2}\right) (1 \pm i\sqrt{3}) + \mathcal{O}(N^{-2}) \quad \forall N \gg N_c$$

$$p^2 \approx -\frac{3(1 \pm 1)}{(N^2\chi^{3/2})^2} \quad \forall N \ll N_c$$  \hspace{1cm} (23)

For $N \gg N_c$, the solution can be taken to be of the form $\sim \exp(-\kappa r) \sin(p'r)/r$, where $p'$ is real, $\bar{b} = 8\,\text{Å}, \chi = 0.02$, $N = 100$ we get $\kappa^{-1} \sim N\bar{b}\chi^{1/2}/(3^{1/2})^{1/2} \sim 50\,\text{Å}$. Thus we
obtain a localized coherent solution, which decays in a predominantly exponential manner in space, and describes the composition of self-assembled domains when $N > N_c$.

The extent of the solution decreases as the chain length gets shorter. As the localized solution decays exponentially, it implies that the concentration of the hard segments is decreasing. In turn, this means that the concentration of the soft segments is increasing in the coronal layer. Thus we find that the hard domains are not made up exclusively of the hard segments of urethane and that soft polyester segments are mixed in the domain.

Given the linearity of the governing equation, it follows that the amplitude of the solution is arbitrary. Thus we can use Eqn. (22) to describe the domains of soft segments distributed within the system. These soft domains, by the preceding argument have hard segments mixed in. Therefore not all hard segments aggregate within hard domains as is believed in the folklore.

Below the onset of self-assembly ($N << N_c$), the solution has a form $\exp(-qr)/r$, with $q = 0$ (long-range), or $q$ is some large real number $\propto N^{-2}$. In either case, there is a singularity at the origin. Thus both roots must be excluded from consideration. And so we do not obtain coherent localized structures for $N < N_c$.

**V. CONCLUSIONS**

We have provided a theory of self-assembly in random copolymers based on what can be described as a density functional approach. This formalism is different than the density functional formalism being developed by Fraaije et al.$^{30}$ That theory begins with an energy functional involving purely the local concentrations of the species, whereas in our approach, a phase appears as well. Our classical mechanics theory is closer in spirit to the Kohn-Sham density functional approach which invokes a (fictitious) wave-function whose square is interpreted as the probability density. With this formalism, we were able to show in a relatively simple manner how to obtain a physical constraint on the segments of the polymers in the system that prevents them from straying too far from each other, and leads to self-
assembly.

Besides the simplicity of our derivation, we have shown that a self-assembling random copolymer system exhibits a transition analogous to the entanglement transition for homopolymer melts as the chain length is increased. The cause for this is the restriction on the motion of the self-assembled aggregates in a thicket of polymer strands.

Our original motivation for this research was to gain an understanding of the mechanical strength of self-assembling random copolymers. We showed in this paper that in contradiction to existing folklore, their mechanical properties originate in the interstitial region between the nanoscale aggregates.

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FIGURES

FIG. 1. Plots of the structure factor for relatively long chain lengths. Note the shift towards larger wavenumbers as the chain length degrades. The abscissa is in units of inverse Å. The other parameters used were \( b = 8 \text{Å}, \chi = 0.02 \). Note that the intercept on the ordinate, which is proportional to the Young's modulus, does not change.

FIG. 2. Plots of the structure factor for relatively short chain lengths. Note the shift towards larger wavenumbers as the chain length degrades for \( N \) between 90 and 100. Below \( N =90 \), the peak actually shifts towards lower wavenumbers. The abscissa is in units of inverse Å. The other parameters used were \( b = 8 \text{Å}, \chi = 0.02 \). The dashed line is an aid to the eye to indicate the flow of the peak location. Note that the intercept on the ordinate, which is proportional to the Young's modulus, does not change.

FIG. 3. Location of the peak as a function of the chain number \( N \). Near the critical chain length \( N_c = 50 \) below which self-assembly cannot take place, note that the peak location is actually increasing with \( N \). Far from \( N_c \), the opposite behavior is found. The dashed line indicates the value of the chain length at which the transition occurs.

FIG. 4. Plot of the natural logarithm of the peak value of the structure factor for estane as the chain length is increased. The minimum in the figure indicates the onset of self-assembly. This minimum does not correspond to the maximum in the previous figure, which pertains to another transition. The maximum in the peak value of the structure factor is attained only asymptotically. The filled square indicates the location of the ODT according to Leibler's theory.
Chitanvis, Fig. 1

$k$ (Inverse Angstroms)

$S(k)$

$N=1000$

$N=800$

$N=750$
Chitanvis, Fig. 2
Chitanvis, Fig. 4