

Physics of polymer melts

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We have mapped the physics of polymer melts onto a time-dependent Landau-Ginzburg $|\psi|^4$ field theory using techniques of functional integration. Time in the theory is simply a label for the location of a given monomer along the extent of a flexible chain. With this model, one can show that the limit of infinitesimal concentration of a polymer melt corresponds to a *dynamic* critical phenomenon. The transition to the entangled state is also shown to be a critical point. For larger concentrations, when the role of fluctuations is reduced, a mean-field approximation is justifiably employed to show the existence of tubelike structures reminiscent of Edwards' model.

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I. INTRODUCTION

Issues in polymer melt physics have continued to provide an enduring source of theoretical investigations, owing to the complexity of the field. The basic physics of flexible polymer melts is embodied in Flory's theorem [1]. This theorem states that at a low number density, fluctuations in the melt are quite pronounced, while for a large density, fluctuations are so suppressed that the polymers behave as independent Gaussian chains again. de Gennes showed [1] that at a low number density, the physics of melts can be mapped onto that of the critical point for ferromagnets. He derived scaling relations for global quantities such as the radius of gyration R_g (end-to-end distance) of a polymer.

One purpose of this paper is to revisit polymer melt physics in the interesting low-density regime. It is shown that the connectivity of the chains in the system implies that the physics can be mapped onto that of a dynamic critical phenomenon [2], rather than a critical point in the static sense [1]. Our estimate of the Flory exponent ν is approximately 0.631, in line with universality arguments, and differs from the usual estimate of 0.588. The new viewpoint also allows a computation of the local structure of individual chains, in addition to the radius of gyration R_g . In the old picture, the radius of gyration R_g was shown to possess a scaling form, while local properties of chains could not be addressed.

Additionally, we show that our technique can be used to describe the onset of entanglement as a critical point in the theory of phase transitions. A study of this transition is beyond the scope of the standard tube model, a mean-field approximation. The physics of the transition from the unentangled to the entangled state has been probed by Schweizer *et al.* [3] using mode-coupling methods. The problem has also been treated more recently by Binder *et al.* [4] using Monte Carlo techniques. These investigations come to the conclusion that the transition to the entangled state is characterized by a slowing down of the polymer dynamics, analogous to a critical slowing down in the theory of phase transitions. Our method could be viewed as a renormalization-group generalization of Schweizer's mode-coupling methods. This paper uses field-theoretic methods to

clarify earlier studies regarding the nature of the critical pointlike transition to the entangled state.

II. A PATH-INTEGRAL APPROACH

The self-consistent field theory (SCF) discussed by de Gennes [1] is a mean-field approximation to study melts of flexible polymers. Generalizing this model beyond its mean-field roots has obvious advantages. Such a generalization has been attempted [5]. However, while this generalization was appropriate for the intended application, it ignored an important property of polymers. The theory involves a description of polymers in terms of a field $\psi(\vec{r})$, where \vec{r} is the location in physical space of any segment, such that $|\psi(\vec{r})|^2$ is the probability of finding a segment at \vec{r} . If the polymer is N segments long, there is no representation in this theory of which segment (1 through N) this field refers to. In other words, reference to the connectivity of the chains is missing. This can be achieved using ideas from functional integration.

The propagator for a single flexible chain may be represented by [6]

$$G_0(1,2;n) \equiv \langle 1,n | \left[\partial_n - \left(\frac{b^2}{6} \right) \nabla^2 \right]^{-1} | 2,0 \rangle \\ \sim \int_{\vec{R}_2}^{\vec{R}_1} \mathcal{D}\vec{R}(n') \exp - \left[\left(\frac{3}{2b^2} \right) \int_0^n dn' \left(\frac{\partial \vec{R}(n')}{\partial n'} \right)_2 \right], \quad (1)$$

where b is the bond length of the polymer, and where $\partial_n \equiv \partial/\partial n$. This expression is obtained by considering only the entropy of a flexible chain.

Alternatively, one knows from methods in functional integration that [7]

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

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

where $\mathcal{D}^2\psi \equiv \mathcal{D}\psi^*\mathcal{D}\psi$, $\beta = 1/k_B T$, k_B is Boltzmann's constant, and T is the temperature. Thus we have another way of thinking about a system of flexible polymers, in terms of $\psi(\vec{x}, n)$, and an energy functional $\beta\mathcal{F}$ that 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, and $|\psi(\vec{x}, n)|^2$ is the probability of finding a polymer segment at a given location in space, as suggested by Eq. (15) below. While Eq. (15) has been derived in the mean-field approximation, we have only considered small perturbations around the mean field, so that the interpretation of $|\psi|^2$ as the probability density is correct in this paper. Consequently, we have a density-functional theory in the sense of Kohn and Sham, which utilizes a *fictitious* wave function such that its absolute value squared yields the *correct* probability density. The important difference between our approach and the Kohn-Sham theory is that we have a classical theory. Kleiner [8] and Semenov *et al.* [9] have proposed similar formalisms. However this paper uses the new formalism to probe the physics of polymer melts in a broader sense.

It is possible to derive from the partition function $\mathcal{Z} = \int \mathcal{D}^2\psi \exp[-\beta\mathcal{F}]$, a $2p$ -point correlation function, which decouples at the noninteracting level into a product of Green's functions for p independent polymers. The main advantage of the functional path-integral formalism is that one can now model more easily interactions in systems with large numbers of polymers. The following model, written to look like a Kohn-Sham-type density-functional theory, describes excluded volume effects:

$$H_0 \rightarrow H = H_0 + V - \mu, \quad (3)$$

$$H_0 \equiv - \left(\frac{b^2}{6} \right) \nabla^2,$$

$$V = \frac{v}{2} |\psi(\vec{x}, n)|^2,$$

where v is the usual excluded volume interaction parameter [6] and μ is the chemical potential invoked in the form of a Lagrange multiplier to conserve the number of polymer segments in the system.

The self-avoiding walk of a solitary chain can be modeled by starting from Eq. (1) [10] by adding to the argument of the exponential on the right-hand side, a series of terms that describe the excluded volume interaction between polymer segments. Caution must be used to apply this approach to a system of many polymers.

To understand the physics in the $|\psi|^4$ model, let us extremize the functional density \mathcal{F} , while considering only solutions homogeneous in space and in n . This yields a maximum at $\psi = 0$ and minima at

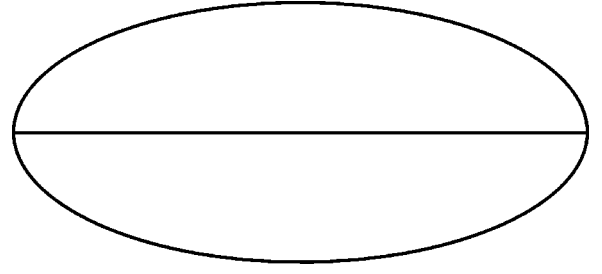


FIG. 1. The Saturn diagram, which makes the first nontrivial contribution to the two-point correlation function.

$$|\psi|^2 = \frac{\mu}{v}. \quad (4)$$

This of course leads to an infinity of solutions, equivalent within a phase difference. Following quantum field theory ideas, the phase of the field can be related to scattering or interaction effects. The physical system can be thought of as localized regions where Eq. (4) is satisfied, separated by domain walls which permit the transition from one minimum to another.

Note that Eq. (4) is equivalent to an estimate of the chemical potential ($\mu_0 = c_0 v$) if the average number density c_0 is known. From this viewpoint, $c_0 \rightarrow 0$ represents a system of polymers that approaches a critical point from *below*. Here we have in mind an analogy with the usual Landau-Ginzburg ϕ^4 model, where the vanishing of the coefficient of the quadratic term in the energy functional leads to a single well potential, signifying a critical point in the phase diagram. This issue was treated by de Gennes by mapping the polymer problem onto one in a zero-component ϕ_j^4 field theory (the self-avoiding walk of a solitary chain) [10]. The different perspective offered by our theory is that the physics of low concentration melts is really an issue in *dynamic* critical phenomena, given the degree of freedom represented by the variable n .

III. DIAGRAMMATIC CORRECTIONS TO THE GAUSSIAN APPROXIMATION

It is necessary to go beyond the Gaussian approximation in the low number density regime because this regime is close to a critical point, as discussed in the preceding section, and fluctuations become important. Diagrammatic methods permit us to go beyond the Gaussian approximation in a perturbative manner. In this way we can gain insight into the local structure of flexible chains in the low-density regime, as well as compute Flory's exponent ν for the radius of gyration.

We can compute a dynamic correction to the free-particle Green's function, from the so-called Saturn diagram shown in Fig. 1 [11,2,12]. This diagram is the lowest-order nonvanishing \vec{k}, ω -dependent contribution to the self-energy. To do this calculation, it is first convenient to write $\beta\mathcal{F}$ in a dimensionless form, using $\psi \rightarrow \psi/\sqrt{c_0}$, and scaling all length scales by $c_0^{-1/3}$. This yields $v \rightarrow \alpha = c_0 v$. In the limit of small μ_0 ,

$$\hat{G}_0(\vec{k}, \omega) \rightarrow [G_0^{-1}(\vec{k}, \omega) - \Sigma(\vec{k}, \omega)]^{-1},$$

$$\Sigma(\vec{k}, \omega) \approx 48\alpha^2 \int \frac{d^3k_1}{(2\pi)^3} \int \frac{d^3k_2}{(2\pi)^3} \frac{1}{-i\omega + (c_0^{-2/3}b^2/6)(\vec{k}_1^2 + \vec{k}_2^2) + (c_0^{-2/3}b^2/6)(\vec{k} - \vec{k}_1 - \vec{k}_2)^2 - 3\mu_0}, \quad (5)$$

where $\hat{G}_0(\vec{k}, \omega)$ is the Fourier transform of the Green's function introduced in Eq. (1), and where we have performed the frequency integrations involved in the diagram using the method of residues and we used the mean-field value for the chemical potential $\mu_0 = c_0 v \rightarrow 0$. This integral can be found in Hohenberg and Halperin [2] and they use Wilson's renormalization scheme to analyze the properties of this integral. We have been able to evaluate this multidimensional integral analytically. The integrals were performed using the identity $1/t = \int_0^\infty d\lambda \exp(-\lambda t)$ and introducing a change of variables to the center-of-mass and relative coordinates of \vec{k}_1, \vec{k}_2 . This allows a separation of variables to occur, permitting an integration over the momentum variables. The last integration is performed using the identity $\int_0^\infty \exp(-Ax)x^k dx = A^{-1-k}\Gamma(1+k)$. Using the method of dimensional regularization [11,12], the final result is

$$\Sigma(\vec{k}, \omega) = \alpha^2 A (2m)^{3-1/C} [-i\omega + k^2/(6m) - 3\mu_0]^2 \times (C - \ln\{2m[-i\omega + k^2/(6m) - 3\mu_0]\}), \quad (6)$$

$$C = \ln[4\sqrt{3}\pi] + \text{diGamma}(3) \approx 4,$$

$$\Sigma(\vec{k}, \omega) \approx \alpha^2 A C (2m)^{3-1/C} [-i\omega + k^2/(6m) - 3\mu_0]^{2-1/C},$$

where $A = 2\sqrt{3}\pi^{-3/2}$ and $m = 3/c_0^{2/3}b^2$. The last approximation in Eq. (6) applies when the argument of the logarithm has a magnitude less than 1. Since $\mu_0 \leq 1$, the approximate scaling form thus holds for $|\omega| \leq 1$ and $k \leq \sqrt{18}/b$, with an error of a few percent or less. In writing down these equations, we have implicitly performed *mass* renormalization [2]. The effect of the self-energy Σ is more pronounced at small length scales than it is at long wavelengths. The renormalized Green's function can also be written for $|\vec{k}| \rightarrow 0$ as

$$\hat{G}(\vec{k}, \omega) \approx \frac{1}{-i\omega + \left(\frac{B^2(\omega, \mu_0)}{6}\right)k^2 - \tilde{\mu}(\omega, \mu_0)}, \quad (7)$$

where

$$\tilde{\mu}(\omega, \mu_0) = \mu_0 - \alpha^2 A (2m)^{3-1/C} (-i\omega - 3\mu_0)^{2-1/C},$$

$$B^2(\omega, \mu_0) = b^2 c_0^{2/3} + \Delta b^2(\omega, \mu_0), \quad (8)$$

$$\Delta b^2(\omega, \mu_0) = -\alpha^2 (6A) (2m)^{3-1/C} (2-1/C) \times (-i\omega - 3\mu_0)^{1-1/C}.$$

Note that this approximation holds in the regime discussed below Eq. (6). Now $-i\omega \equiv \partial/\partial n \sim 1/|p-q|$, with p, q referring to the p th and q th segments, respectively, while k is the inverse separation in physical space of these segments. In the vicinity of the critical point $\mu_0 = 0$, Δb^2 displays a scaling property, viz., $\sim -|p-q|^{-\sigma}$ in the appropriate regime, where we have defined a scaling exponent σ ,

$$\sigma = (1-1/C) \sim 0.75. \quad (9)$$

In this regime, the coefficient of the scaling term behaves as $\sim \alpha^{0.2}$, a weak dependence, if we estimate $v \sim b^3$.

It follows from Eq. (8) that the effect of the gradient-smoothing term ∇^2 in the energy functional is reduced by an amount $-|\Delta b^2|$, and this effect is dominant for segments separated by a relatively short distance, as it vanishes in the limit of infinite separation. It means that if segments on a chain happen to be in close proximity in the melt, they will tend to stay together due to the reduction of the smoothing term. Neutron-scattering experiments or numerical simulations may provide verification of this notion. Neutron experiments are customarily employed in the long-wavelength regime to investigate quantities such as the radius of gyration of polymeric systems. Other techniques, such as those used by Smith *et al.* [13], may be more useful.

The chain takes on the appearance of pearls on a string that push the ends of the string further away from each other. One way to calculate the scaling properties of the radius of gyration within the current model is to compute vertex corrections within the current model, and then implement Wilson's scaling arguments. However, it is easier to go back to the original theory defined by the energy density $\psi^*(\partial_n + H)\psi$ and truncate it with $\partial_n \rightarrow 1/N$, where N is the average chain length of the polymeric system. This is justified on the grounds that we are interested only in long-range fluctuations. Accordingly, we also have to restrict the n' integration in $\beta\mathcal{F}$ to a small neighborhood around N . After performing this renormalization, the entire machinery of the static theory of critical phenomena applies. And it follows that very near the critical point $\mu_0 = 0^+$ and the correlation length $\xi \equiv R_g \sim N^\nu$, where the lowest-order field-theoretic techniques yield $\nu \approx 0.6$, the value obtained by Flory.

More accurate calculations yield [6] a value for ν closer to 0.631 [8,11]. The standard model for examining the effects of excluded volume interactions yields [14] $\nu \approx 0.588$. The difference between this model and ours was discussed below Eq. (3).

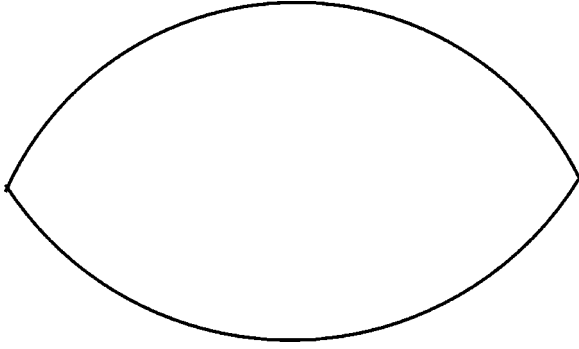


FIG. 2. The fish diagram, which makes the first nontrivial contribution to the vertex correction.

IV. APPROACH TO ENTANGLEMENT

As the number density of chains in a melt begins to increase, there is a transition to an entangled state at some value of the number density $c_0 < 1/v$. To see this, let us begin by computing vertex corrections, which can be thought of as giving rise to an effective coupling constant. The physical idea behind the computations is to show perturbatively that as the number concentration increases, the effective coupling constant actually decreases. This is in accordance with Flory's theorem for polymer melts, which states that as the number density increases, the polymers begin to behave as free chains again. But we shall go beyond the theorem in showing that the effective coupling constant decreases in consonance with the renormalization-group theory of phase transitions and possesses a fixed point. By this we mean that at a critical number density, the changes in the effective coupling constant are independent of the relevant length scale, analogous to the behavior of a liquid at its critical point. This conclusion clarifies the investigations Schweizer [3] and Binder [4] by characterizing the transition to the entangled state as a continuous, second-order phase transition.

The lowest-order correction comes from the so-called fish diagram (see Fig. 2) with two internal lines. The frequency integral involved in the calculation is performed by closing the contour in the upper half-plane. Using standard renormalization techniques [11] leads to a renormalized coupling constant α_R :

$$\alpha_R(q) = \alpha - \alpha^2 \bar{\Gamma}(q), \quad (10)$$

$$\bar{\Gamma}(q) \approx \left(\frac{(6\mu_0)^{3/2}}{24\pi^2 c_0 b^3} \right) \frac{1}{-i\omega_q - 2\mu_0 + \vec{q}^2/2m} + O(\vec{q}^2),$$

where $q \equiv (\vec{q}, \omega_q)$. Notice that to this order in perturbation theory, an increasing concentration signified by an increasing α ($= c_0 v$) leads to a lower effective coupling constant, consistent with the latter half of Flory's theorem. We can now define a beta function as is done conventionally in renormalization-group theory. The role of the beta function is to measure the sensitivity of the renormalized coupling constant to the relevant length scale:

$$\beta(\hat{\alpha}_R) = \frac{\partial \hat{\alpha}_R}{\partial \ln y} \approx -\hat{\alpha}_R + \hat{\alpha}_R^2,$$

$$y = -i\omega_q - 2\mu_0 \equiv 1/N - 2\mu_0, \quad (11)$$

$$\hat{\alpha}_R \equiv \left(\frac{(6\mu_0)^{3/2}}{24\pi^2 c_0 b^3} \right) \alpha_R(\vec{q}=0),$$

where $y \equiv 1/N - 2\mu_0$ plays the role of a scaling parameter, equivalent to an inverse length scale. As $y \rightarrow 0$ [$N \rightarrow (2\mu_0)^{-1}$], we see that there is a nontrivial fixed point at $\hat{\alpha}_R = 1$ when the beta function vanishes. For $\hat{\alpha}_R < 1$, $\beta < 0$, so that in the long-wavelength limit, as $y \rightarrow 0$, the renormalized constant flows towards the fixed point. Similarly for $\hat{\alpha}_R > 1$, $\beta > 0$, so that the renormalized constant again flows towards the fixed point. Therefore, in the language of renormalization-group theory, this is an infrared *stable* fixed point. In other words, the long-wavelength behavior of the system is dominated by $\hat{\alpha}_R = 1$ and is independent of the microscopic details of the Hamiltonian. In this sense, our fixed point is analogous to the conventional critical point in phase-transition theory.

This fixed point can be identified with the transition of a system of flexible polymers from an unentangled state to an entangled state. We offer evidence below in support of this concept.

As an example, it can be checked in the case of polydimethylsiloxane (PDMS) that $c_0 \sim 3 \times 10^{-3} \text{ cm}^{-3}$, $b \sim 1.5 \text{ \AA}$, yielding $N_c \sim 167$, which is close to the experimentally determined [15] critical entanglement chain length of ~ 200 . Similarly, for polystyrene, using $b \sim 1 \text{ \AA}$, we get $N_c \sim 320$, reasonably close to the critical chain length estimated by the viscosity measurements of Onogi *et al.* [16]. To the lowest order, the structure factor $\hat{S}(q) = (2/3)\bar{\Gamma}(q)$. It diverges as $|\vec{q}|^{-2}$ at $y=0$, analogous to the behavior at a critical point. The Young's modulus Y of the system is given by [17] $Y \propto \hat{S}(\vec{q}=0, \omega)$, and it will show a dramatic rise as the chain length N is increased towards N_c for $\mu_0 \neq 0$. For these reasons we can identify this critical-like point with the onset of entanglement. Note that the approximation to $\hat{S}(q)$ we have used here will not work past the transition to entanglement. There is some indication of fluctuating behavior near the entanglement transition in the classic viscoelasticity measurements of Onogi *et al.* [16], as indicated by earlier phenomenological analyses [17,18].

V. TUBE-LIKE STRUCTURES IN THE ENTANGLED STATE

Fluctuations in the system tend to decrease as c_0 increases away from the critical point just discussed. So for finite concentrations we expect mean-field theory to hold. In this limit, we get a time-dependent Landau-Ginzburg equation (time $\equiv n$), by extremizing $\beta\mathcal{F}$ with respect to ψ^* :

$$\left[\frac{\partial}{\partial n} - \left(\frac{b^2}{6} \right) \nabla^2 - \mu_0 + v |\psi(\vec{x}, n)|^2 \right] \psi(\vec{x}, n) = 0. \quad (12)$$

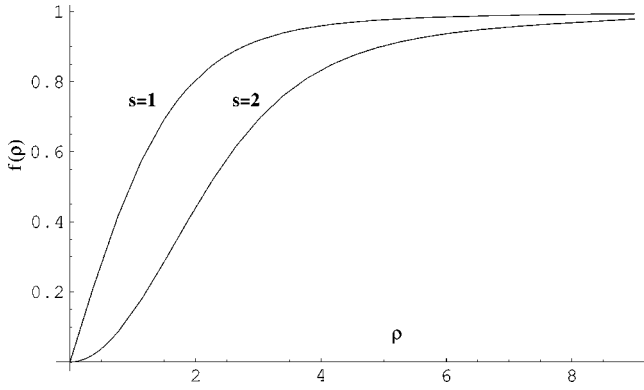


FIG. 3. Numerical solutions of Eq. (13) for $s=1$ and $s=2$. Both curves asymptote to unity, but on different scales.

For the moment, let us suppose that there is no n dependence in ψ . Then the model reduces to the SCF equation. Noting the similarity of this equation to the one used to describe bosonic fluids [19], we seek tubelike solutions in cylindrical geometry, viz., $\psi(\rho, \phi) = \exp(is\phi)f(\rho)$, where s is an integer:

$$\frac{1}{\rho} \frac{d}{d\rho} \left(\rho \frac{df(\rho)}{d\rho} \right) + \left(1 - \frac{s^2}{\rho^2} \right) f(\rho) - f^3(\rho) = 0, \quad (13)$$

where ρ has been made dimensionless by the length scale

$$a = b/\sqrt{6c_0v}. \quad (14)$$

We see that for $\rho \rightarrow 0$, assuming $|f(\rho)| \rightarrow 0$, we get a solution proportional to $J_s(\rho) \sim \rho^s$ [19]. By choosing the amplitude of this solution correctly, one can match it for large ρ to a constant solution $f(\rho) = \pm \sqrt{1 - s^2/\rho^2}$ (see Fig. 3). This solution may also be continued mathematically to $s \rightarrow 0$. But then the $s=0$ solution has an infinite slope at the origin. The radial extent of these solutions is $\sim sa$ for $s \neq 0$. From excluded volume considerations, the maximum density possible in the system is $1/v$, and for densities approaching $1/v$, $a \sim b/\sqrt{6}$. Physically, these solutions are reminiscent of the tube model of Edwards [6]. They indicate that the tubes are not empty, but have a concentration of polymers given by $[f(\rho)]^2$. It may be possible to use numerical simulations to check if the qualitative features of the occupation profile $[f(\rho)]^2$ can be reproduced [20].

As discussed by Fetter, the higher the value of s , the higher the energy of the tubelike configuration, and the system will prefer to have many tubes with a low s rather than a few with a large s . We have thus derived from our theory a tube model with a tube radius a , which is exceedingly large for small densities, and asymptotes smoothly in an inverse square root fashion to $\sim b/\sqrt{6}$ as the density approaches $1/v$. Since the monomer length b is of the order of a few angstroms, the magnitude of the tube radius for $c_0v \sim 10^{-2}$ is a few monomer lengths. This is in qualitative agreement with estimates that can be found in the literature [6].

In the theory of superfluids [19], these cylindrical structures are viewed as idealizations of vortices, caused by the rotation of the fluid. In our case we can derive an equation of continuity from Eq. (12):

$$\begin{aligned} \frac{\partial |\psi|^2}{\partial n} &= -\vec{\nabla} \cdot \vec{j} + S, \\ \vec{j} &= \left(\frac{b^2}{6} \right) (\psi^* \vec{\nabla} \psi + \text{c.c.}), \\ S &= \left(\frac{b^2}{3} \right) |\vec{\nabla} \psi|^2 + 2\mu_0 |\psi|^2 - v |\psi|^4. \end{aligned} \quad (15)$$

It follows by examining the current \vec{j} that the tubelike solutions are not caused by rotation, but rather there is a *radial velocity* due to the ρ dependence of the solution. There is yet another solution to Eq. (12), which is obtained by assuming that it is dependent solely on n , which yields $\psi(n) = [1 + \exp(-2n\alpha)]^{-1/2}$. More general solutions can undoubtedly be found numerically by studying Eq. (12) with various boundary conditions.

We speculate that the phase of the field ψ may be useful in quantifying the notion of entanglement in polymers. Ultimately the theory needs to be generalized to handle polymer dynamics.

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