Field Theory of Polymers: Escaping the Sign Problem

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Abstract

We examine statistical field theories of polymeric fluids in view of performing numerical simulations. The partition function of these systems can be expressed as a functional integral over real density fields. The introduction of density field variables serves to decouple interactions among non-bonded monomers, and renders the resulting effective Hamiltonian $H$ for the field theory real and the Boltzmann factor $\exp(-H)$ positive definite. This is in contrast with conventional (Edwards type) field theories expressed in terms of chemical potentials that have complex $H$. The density field theory involves the calculation of an intermediate functional integral, which provides the entropy of the polymer fluid at a fixed density profile. This functional integral is positive definite and we show that in the thermodynamic limit of large systems, it is dominated by saddle points of the integrand. This procedure side-steps the “sign problem” in the chemical potential field formulation. The formalism is illustrated in the context of models of flexible polymers. We discuss the implications for field-theoretic computer simulations of polymeric fluids.

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I. INTRODUCTION

Field theories have proved to be a useful theoretical framework for studying the equilibrium and time-dependent properties of a wide variety of complex fluid systems. In the 1960s, Edwards introduced field-theoretic methods to the field of polymer physics and applied these techniques fruitfully to examine the universal aspects of chain conformational statistics and thermodynamic properties of polymer solutions \[1\]. Perturbation methods, mean-field approximations, and variational schemes were introduced for tackling important problems such as the excluded volume effect and addressing collective phenomena, such as screening in semi-dilute solutions. These analytical methods were considerably enhanced in the 1970s and 1980s with the advent of renormalization group theory, the introduction of scaling concepts, and the discovery of the connection of polymer statistical mechanics with the $n$-vector field theory model for $n \rightarrow 0 \[2\]$. 

Unfortunately, most of these analytical techniques are difficult to apply in the important case of inhomogeneous polymers, which include multicomponent polymer alloys, block and graft copolymers, nano-composites, thin films, emulsions, and suspensions. Appropriate field theory models for such systems are straightforward to construct, but the analytical tools available for examining the properties of the models are rather limited. One powerful tool is self-consistent field theory (SCFT), which amounts to a saddle point approximation to the partition function of the field theory \[3, 4\]. However, the SCFT field equations determining the “mean fields” are nonlinear, nonlocal, and defy analytical solution. Certain limiting cases of SCFT, such as weak inhomogeneities or fields that vary slowly over the size of a polymer, and for simple geometries, are analytically tractable. In such special circumstances, however, the SCFT solutions still reflect the mean-field assumption intrinsic to the theory, which further restricts their applicability. In particular, such solutions are primarily limited to the description of concentrated solutions or melts of high molecular weight polymers. Even in the case of dense molten blends or copolymers, SCFT can fail in situations where soft modes appear, such as near critical points, unbinding transitions, or in micellar or microemulsion phases \[5\], since thermally-induced field fluctuations can then be significant.

In recent years, it has become apparent that field theory models of polymers and complex fluids, besides serving as the platform for analytical calculations, can also provide a flexible
framework for numerical simulations [6]. Building on significant advances in numerical methods for solving the mean-field SCFT equations [7, 8], techniques have been developed for direct numerical sampling of field fluctuations [6, 9]. These methods open many exciting possibilities for carrying out “field-theoretic simulations” of a wide variety of inhomogeneous polymer systems. Aside from the numerical errors associated with representing the fields and the usual statistical errors intrinsic to any computer simulation technique, field-theoretic simulations provide a route to studying the exact properties of a polymer fluid model in the absence of any simplifying approximations. Such field-based simulations also facilitate systematic coarse-graining, making it possible to equilibrate much larger systems with a broader range of structural scales than in conventional atomistic computer simulations. At the present time the methods are limited to equilibrium structure and properties, although research is underway to extend them to nonequilibrium situations.

A difficulty with the current strategies for field-based simulations of polymeric fluids is that they rely on the introduction of Hubbard-Stratonovich “chemical potential” fields, first employed for polymers by Edwards [1], to decouple the non-bonded interactions among monomers. This allows one to explicitly trace out the monomer coordinates in favor of the introduced fields, generating a field theory model for a polymer solution or melt. Unfortunately, this description leads to an effective Hamiltonian $G(\phi)$, expressing the energy of a chemical potential field configuration $\phi(r)$, that is complex, rather than real. As a consequence, the Boltzmann factor $\exp(-G)$ is not positive definite, so conventional Monte Carlo sampling of the partition function is problematic [10]. This difficulty in sampling field configurations is a special case of a more general “sign problem”, which involves the development of techniques for efficient numerical evaluation of high dimensional integrals with non-positive definite integrands. While promising new methods have appeared for battling the sign problem [11, 12], the problem is by no means “solved”. Oscillations in the phase factor $\exp(-i \text{Im} G)$ severely limit the convergence of field-based simulations of polymeric fluids.

In the present paper, we describe an alternative formulation of polymer field theory that essentially side-steps the sign problem. Rather than retaining just a Hubbard-Stratonovich chemical potential field for each monomer species, we also retain a second density field. This two field approach is not new [8, 13], but rather is a usual starting point for deriving SCFT. However, we show in the present paper that at a fixed value of the density field, the
functional integral over the chemical potential field can be performed in the saddle point
approximation, and that this approximation is exact in the thermodynamic limit of large
systems. This we believe to be a new result and one that has profound consequences for
field-theoretic computer simulations of polymeric fluids.

II. BASIC FORMALISM: POLYMER SOLUTIONS

A. Transformation to a Field Theory

Consider a solution of $M$ homopolymer chains in a volume $V$, each chain composed of
$N$ monomers of size $a$. The solvent is not considered explicitly, the temperature is denoted
by $T$, and $\beta = 1/T$. The formalism presented below can be easily generalized to blends of
different chains and to melts or solutions of copolymers as will be seen later.

We assume that the monomers interact through a 2-body interaction potential (of mean
force) denoted by $v(r)$. In the celebrated Edwards model, the interaction $v(r)$ is modelled
as a Dirac delta function, $\delta(r)$, but in general, the interaction $v$ can represent both sol-
vent effects, electrostatic effects or any other effective monomer-monomer interaction. The
canonical partition function of the system reads

$$Z = \frac{1}{M!} \int \prod_{k=1}^{M} D r_k \exp \left( -\frac{3}{2a^2} \sum_{k=1}^{M} \int_0^N ds \left( \frac{dr_k}{ds} \right)^2 - \frac{\beta}{2} \sum_{k,l=1}^{M} \int_0^N ds \int_0^N ds' v(r_k(s) - r_l(s')) \right)$$

(1)

where $\int D r_k$ denotes a path integral over all conformations of the $k$th polymer chain.

Next, we introduce a monomer (number) density field $\hat{\rho}(r)$ as a new integration field.
The microscopic expression for the monomer density, $\hat{\rho}(r)$, is given by

$$\hat{\rho}(r) = \sum_{k=1}^{M} \int_0^N ds \delta(r - r_k(s))$$

(2)

If we constrain $\rho(r)$ to $\hat{\rho}(r)$ at each point $r$ of space by the use of a $\delta$-function, the partition
function of the polymer system can be written as

$$Z = \int D \rho \exp \left( -\frac{\beta}{2} \int drdr' \rho(r)v(r-r')\rho(r') \right) Z(\rho)$$

(3)
where the function $Z(\rho)$ is defined by

$$Z(\rho) = \frac{1}{M!} \int \mathcal{D}r_k \exp \left( -\frac{3}{2a^2} \sum_{k=1}^{M} \int_{0}^{N} ds \left( \frac{dr_k}{ds} \right)^2 \right) \prod_{r} \delta(\rho(r) - \hat{\rho}(r))$$

and $\int \mathcal{D}\rho$ denotes a functional integral over the real, scalar density field $\rho(r)$. The object $Z(\rho)$ is the partition function of a set of $M$ continuous Gaussian chains of $N$ monomers, constrained in such a way that the total monomer density is fixed to $\rho(r)$ at any point $r$ of space. This partition function evidently counts the total number of chain conformations that are consistent with the density profile $\rho(r)$. We thus write

$$Z(\rho) = \exp[S(\rho)]$$

and identify $S(\rho)$ with the entropy of a system of $M$ chains constrained to have a density profile $\rho(r)$. From its very definition, it is clear that $Z(\rho)$ is real and positive for any real $\rho(r)$. In addition, we expect $Z(\rho)$ to scale with $V$, $N$, and $M$ as $(Vg^N)M/M!$, where $V$ is the volume of the system and $g$ is some positive, real constant.

At this stage, it is clear that we have expressed the partition function of the polymeric system in terms of a functional integral over a real field with a positive definite Boltzmann weight. We have yet to show how to compute the entropic part of the weight, namely the factor $Z(\rho)$.

Using a Fourier representation of the delta function, the above expression for $Z(\rho)$ can be written as

$$Z(\rho) = \frac{1}{M!} \int \mathcal{D}\phi \exp \left( i \int dr \phi(r)\rho(r) + M \ln Q(i\phi) \right)$$

where

$$Q(i\phi) = \int \mathcal{Dr} e^{-\frac{a^2}{2\hbar} \int_{0}^{N} ds (\frac{d\phi}{ds})^2 - i \int_{0}^{N} ds \phi(r(s))}$$

is the partition function of a single polymer in the presence of the potential $i\phi(r)$. It is important to note that this is a purely imaginary potential because the functional integral in eq. (6) is over a real field $\phi(r)$. We recognize in eq. (7) a Feynman path integral for a quantum mechanical problem with quantum Hamiltonian $\mathcal{H} = -\frac{a^2}{6} \nabla^2 + i\phi(r)$. Using standard quantum mechanical notation, we may write

$$Q(i\phi) = \int dr \int dr' < r | e^{-N\mathcal{H}} | r' >$$
B. Expansion about the Saddle Point

Of particular interest is an asymptotic expansion of $Z(\rho)$ for large $M$ to examine the thermodynamic limit of $M \to \infty, V \to \infty, \ M/V$ finite. For this purpose, we perform a saddle point expansion of the $\phi$ integral. The first step is to write an equation for the mean-field (saddle point) $\phi_0(r)$ that produces the desired $\rho(r)$

$$\rho(r) = -M \frac{\delta \ln Q(i\phi_0)}{\delta(i\phi_0(r))}$$  \hspace{1cm} (9)

$$= \frac{M}{Q(i\phi_0)} \int_0^N ds \ \Psi(r,s) \Psi(r,N-s)$$ \hspace{1cm} (10)

Here, $s$ is denotes a contour location along the chain and the “propagator” $\Psi(r,s)$ satisfies the diffusion equation (analogous to the Schrödinger equation)

$$\left( \frac{\partial}{\partial s} - \frac{a^2}{6} \nabla^2 + i\phi_0(r) \right) \Psi(r,s) = 0$$ \hspace{1cm} (11)

subject to the initial condition $\Psi(r,0) = 1$. The single chain partition function is related to the field $\Psi$ by

$$Q(i\phi) = \int dr \ \Psi(r,N)$$ \hspace{1cm} (12)

From the structure of the above equations, we can make a few general statements. First, a necessary condition for eq. (9) to have a solution $\phi_0(r)$ is that $\rho(r)$ should be positive at any point $r$ and that its integral over space should be equal to $MN$. It is also clear from eqs. (9) and (10) that a self-consistent solution may exist with a real $i\phi_0(r)$, i.e. purely imaginary $\phi_0(r)$. From the structure of these equations, we see that if $\phi_0(r)$ is a mean-field (saddle point) solution, one can add to it any constant and obtain a new solution. To lift this degeneracy of the saddle-point, we may specify the value of the field $\phi_0$ at a specific point in space, or its spatially-averaged value. Having made such a choice, it can be proven that such a real solution $i\phi_0(r)$ not only exists, but is a unique solution of the above equations.

To perform the asymptotic expansion about the saddle point $\phi_0$ at higher orders, we shift the integration variable $\phi$ by writing

$$\phi(r) = \phi_0(r) + \chi(r)$$

The partition function then reads

$$Z(\rho) = Z_0(\rho) \int D\chi \ \exp \left( i \int dr \ \chi(r) \rho(r) + M \ln Q(i\chi) \right)$$ \hspace{1cm} (13)
where

\[
Q(i\chi) = \frac{\int \mathcal{D}r \, e^{-\frac{i}{2\sigma} \int_0^N ds \left( \frac{\partial}{\partial r} - i \int_0^N ds \phi_0(r(s)) - i \int_0^N ds \chi(r(s)) \right)^2}}{\int \mathcal{D}r \, e^{-\frac{i}{2\sigma} \int_0^N ds \left( \frac{\partial}{\partial r} - i \int_0^N ds \phi_0(r(s)) \right)^2}}
\]  

(14)

and \(Z_0\) denotes the mean-field value of the partition function

\[
Z_0(\rho) = \frac{1}{M!} \exp \left( i \int dr \phi_0(r) \rho(r) + M \ln Q(i\phi_0) \right)
\]  

(15)

Next, we expand the exponent in the integrand of eq. (13) in powers of \(\chi\). For this purpose, it is convenient to reexpress eq. (14) as

\[
Q(i\chi) = \langle e^{-i \int_0^N ds \chi(r(s))} \rangle_0
\]  

(16)

where the notation \(\langle ... \rangle_0\) describes the expectation value over the conformations of a single polymer subjected to the mean-field potential \(i\phi_0\). Expanding in powers of \(\chi\) and rescaling the field \(\chi\) by a factor of \(\sqrt{M}\), we obtain

\[
Z(\rho) = Z_0(\rho) \int \mathcal{D}\chi \, \exp \left( -\frac{1}{2} \int dr dr' \chi(r)G_2(r, r')\chi(r') + W(\chi) \right)
\]  

(17)

where

\[
W(\chi) = \sum_{p=3}^{\infty} \frac{(-i)^p}{p! M^{p/2-1}} \int dr_1 \ldots dr_p \chi(r_1) \ldots \chi(r_p)G_p(r_1, \ldots, r_p)
\]  

(18)

and \(G_p(r_1, \ldots, r_p)\) denotes the \(p\)-point connected (cumulant) correlation function for the density of a single chain, defined by

\[
G_p(r_1, \ldots, r_p) = \langle \tilde{\rho}(r_1) \ldots \tilde{\rho}(r_p) \rangle_c
\]  

(19)

where \(\tilde{\rho}(r) = \int_0^N ds \delta(r - r(s))\) is the single chain microscopic density. This expectation value is taken with respect to the conformations of a single chain in the mean-field according to eq. (16) with the usual definition of connected averages [14]. Note that there is no linear term in \(\chi\) appearing in the exponent of eq. (17) since the action is stationary with respect to \(\phi_0\).

The partition function of eq. (17) can be calculated in a perturbation expansion in powers of \(1/M\). This is most conveniently done by the use of Feynman diagrams in which propagator lines are associated with factors of \(S_2(r, r') = G_2^{-1}(r, r')\) and \(p\)th-order vertices are assigned factors of \([(-i)^p/M^{p/2-1}]G_p(r_1, \ldots, r_p)\). The result is that

\[
Z(\rho) = Z_0(\rho) \exp \left( -\frac{1}{2} \text{Tr} \ln G_2(r, r') + \text{Sum of all Connected Diagrams} \right)
\]  

(20)
where the connected diagrams have one or more vertices of degree \( p \geq 3 \). Since the vertices in eq. (19) are connected correlation functions, all terms in the exponent of eq. (20) are extensive, that is they are proportional to the volume \( V \) of the system. The general expansion of \( Z(\rho) \) thus takes the form

\[
Z(\rho) = \exp \left[ -\beta V \left( f_0 + \frac{f_1}{M} + \frac{f_2}{M^2} + \ldots \right) \right]
\]

where the \( f_j \) are contributions to the free energy density that are independent of \( M \) and \( V \) in the thermodynamic limit. Since all vertices carry powers of \( 1/M \), the sum of all connected graphs is negligible in the thermodynamic limit, and eq. (20) yields

\[
Z(\rho) \simeq Z_0(\rho) \exp \left( -\frac{1}{2} \text{Tr} \ln G_2(r, r') \right)
\]

in the limit \( M \to \infty \). We note that \( G_2(r, r') \) is a functional of \( \rho \), because it represents the 2-point connected correlation function of a chain subjected to the mean-field potential \( i\phi_0 \) and \( \phi_0 \) is in turn related to \( \rho \) by the saddle point condition eqs. (9)-(10).

From the form of eq. (22), it would appear that there is a correction to the mean-field value \( Z_0(\rho) \) of the restricted density partition function \( Z(\rho) \) that is associated with Gaussian fluctuations in \( \chi(r) \) about the mean chemical potential field \( \phi_0(r) \). Interestingly, these corrections from Gaussian field fluctuations play no role in the statistical properties of the field \( \rho \) for \( M \to \infty \). This is demonstrated by two independent routes in the next section.

**C. Significance of the Fluctuation Term**

To examine the significance of the fluctuation term \( \frac{1}{2} \text{Tr} \ln G_2(r, r') \), we return to the original formulation of the field theory prior to the asymptotic expansion in \( M \). From eq. (3) it is clear that we can write an effective, real field theory for the \( \rho \) field as

\[
Z = \int \mathcal{D}\rho \ exp[-H(\rho)]
\]

where the effective Hamiltonian \( H(\rho) \) is given by

\[
H(\rho) = \frac{\beta}{2} \int drdr' \rho(r)v(r-r')\rho(r') - S(\rho)
\]

where \( S(\rho) = \ln Z(\rho) \) is given in eq. (6). One way to simulate such a field theory is through a Langevin stochastic dynamics [15] for \( \rho \). Note that the density field \( \rho(r) \) is constrained
to be positive at each point $r$. A simple way to enforce this condition in the functional integral (23) is to add an external potential which is infinite when $\rho(r)$ is negative and 0 when $\rho(r)$ is positive. A practical realization of such a potential can be obtained by adding an exponential function to the Hamiltonian, and define

$$H'(\rho) = H(\rho) + \int dr \ e^{-\lambda \rho(r)}$$

where $\lambda$ is a constant, chosen large enough to ensure the positivity constraint.

If we keep in mind that the total number of monomers is fixed, equal to $MN$, we may use the conserved dynamics (model B) and write

$$\frac{\partial}{\partial t} \rho(r, t) = \Gamma \nabla^2 \delta H' \delta \rho(r, t) + \eta(r, t)$$

(25)

where we have used

$$\frac{\delta S(\rho)}{\delta \rho(r, t)} = \frac{\delta \log Z(\rho)}{\delta \rho(r, t)} = < i\phi(r, t) > _\rho - \lambda e^{-\lambda \rho(r)} + \eta(r, t)$$

(26)

The Laplacian in front of the r.h.s. of (25) ensures that the space integral of $\rho(r, t)$, which is equal to the total number of monomers $MN$, remains constant in time. In the above equation, the expectation value $< i\phi(r) > _\rho$ denotes an equilibrium average of the field $i\phi(r)$ at constrained $\rho(r)$ using the statistical weight contained in eq. (6) for $Z(\rho)$.

With the use of eq. (17), it is easily seen that

$$< i\phi(r) > _\rho = i\phi_0(r) + \frac{i}{\sqrt{M}} < \chi(r) > _\rho$$

where

$$< \chi(r) > _\rho = \int D\chi \chi(r) \exp \left( -\frac{1}{2} \int dr dr' \chi(r) G_2(r, r') \chi(r') + W(\chi) \right)$$

$$\int D\chi \exp \left( -\frac{1}{2} \int dr dr' \chi(r) G_2(r, r') \chi(r') + W(\chi) \right)$$

and $W(\chi)$ is given by eq. (18). From this expression it follows immediately that

$$< i\phi(r) > _\rho = i\phi_0(r) + O\left( \frac{1}{M} \right)$$

(27)
and thus, in the Langevin equation formalism, it is sufficient to evaluate \( <i\phi(r)>_\rho \) at the mean-field level to capture the leading asymptotic behavior in the thermodynamic limit. The evaluation of the Langevin forces on the right hand side of eq. (25) therefore requires only the computation of \( \phi_0(r,t) \), which follows from the solution of the saddle point equations at prescribed \( \rho(r,t) \). The forces entering the Langevin equation are real (since \( i\phi_0 \) is real), and thus we have a conventional real Langevin dynamics. The key result is that in the thermodynamic limit, there is no signature of the fluctuation term \( (1/2)\text{Tr} \ln G_2(r,r') \) that appears in eq. (22) for \( Z(\rho) \).

The same result can be directly obtained from eq. (22) by means of some straightforward manipulations. Indeed, from that equation and eq. (15), we have

\[
\frac{\delta \ln Z(\rho)}{\delta \rho(r_0)} = <i\phi(r_0)>_\rho \tag{28}
\]

\[
= i\phi_0(r_0) - \frac{1}{2} \frac{\delta \text{Tr} \ln G_2(r,r')}{\delta \rho(r_0)} \tag{29}
\]

The \( \text{Tr} \ln \) term can be further simplified. Using some simple identities, we get

\[
\frac{\delta \text{Tr} \ln G_2(r,r')}{\delta \rho(r_0)} = \int dr dr' \frac{\delta G_2(r,r')}{\delta \rho(r_0)} G_2^{-1}(r',r) \tag{30}
\]

\[
= \int dr dr' dr_1 \frac{\delta (i\phi_0(r_1))}{\delta \rho(r_0)} \frac{\delta G_2(r,r')}{\delta (i\phi_0(r_1))} G_2^{-1}(r',r) \]

From our previous definitions, we see that

\[
\frac{\delta G_2(r,r')}{\delta (i\phi_0(r_1))} = -G_3(r,r',r_1) \tag{31}
\]

and the saddle point condition implies

\[
\frac{\delta (i\phi_0(r_1))}{\delta \rho(r_0)} = -\frac{1}{M} G_2^{-1}(r_1, r_0) \tag{32}
\]

Substitution of these results into eq. (30) leads to a final expression

\[
\frac{\delta \ln Z(\rho)}{\delta \rho(r_0)} = i\phi(r_0) - \frac{1}{2M} \int dr dr' dr_1 G_2^{-1}(r_1, r_0) G_3(r,r',r_1) G_2^{-1}(r',r) \tag{33}
\]

Again, since \( G_2 \) and \( G_3 \) are connected Green’s functions, the triple integral in eq. (33) is finite in the thermodynamic limit (non extensive) and this shows that to leading order in \( 1/M \), the expectation value of \( \phi \) is given by its mean-field value \( \phi_0 \), in agreement with eq. (27). In addition, it is easy to see that the correction term calculated here is exactly the same as the one that would have been obtained as the leading term of the perturbation
expansion using eq. (17). We conclude that the fluctuation term $(1/2) \text{Tr} \ln G_2(r, r')$ can be safely omitted from the effective Hamiltonian $H(\rho)$ when computing the Langevin force $\delta H/\delta \rho$ for the purpose of simulating large systems. Moreover, it follows that the fluctuation correction can also be dropped from the Hamiltonian itself, if Monte Carlo simulations are to be employed.

We summarize with the statement that in the thermodynamic limit of large systems, the field theory expressed in density variables can be written as

$$Z = \int \mathcal{D}\rho \exp[-H'(\rho)] \quad (34)$$

with

$$H'(\rho) = \frac{\beta}{2} \int dr dr' \rho(r)\rho(r') + \int dr e^{-\lambda \rho(r)} - \int dr i\phi_0(r)\rho(r) - M \ln Q(i\phi_0) \quad (35)$$

and where the real field $i\phi_0(r)$ is obtained at a particular $\rho(r)$ by the solution of eq. (9).

D. Langevin Dynamics and Monte Carlo: Implementation

The Langevin equation (25) can be discretized both in time and space. A variety of time integration schemes for such nonlinear stochastic differential equations are available [17]. It is of interest to compare this real Langevin scheme with the complex Langevin scheme that has been used to numerically simulate field theories of polymer solutions and melts expressed in chemical potential [i.e. $\phi(r)$] variables [9, 18]. Because the effective Hamiltonian $G(\phi)$ in such field theories is complex, one must address the sign problem. A useful strategy, originally devised by Parisi and Klauder [19, 20], has been to extend the field variables to the complex plane ($\phi = \phi_R + i\phi_I$) and write a Langevin dynamics

$$\frac{\partial}{\partial t} \phi_R(r, t) = -\Gamma \text{Re} \frac{\delta G}{\delta \phi(r, t)} + \eta(r, t) \quad (36)$$

$$\frac{\partial}{\partial t} \phi_I(r, t) = -\Gamma \text{Im} \frac{\delta G}{\delta \phi(r, t)} \quad (37)$$

where $\eta(r, t)$ is a real Gaussian, white noise with the following covariance

$$< \eta(r, t)\eta(r', t') > = 2\Gamma \delta(r - r')\delta(t - t') \quad (38)$$

This procedure, if it converges [12, 21, 22, 23], will properly describe the stationary fluctuation spectrum of a model with complex $G(\phi)$. We have found it to be reasonably effective.
at suppressing phase oscillations in simulations of polymer solutions and melts, although sign problem is still very pronounced in dilute and semidilute systems. An advantage of eqs. (36)-(37) is that the computation of the complex force $\delta G/\delta \phi$ requires only a single pass at solving the diffusion equation (11) (with $\phi_0 \to \phi$), while computation of $\delta H'/\delta \rho$ in the real Langevin scheme of eq. (25) requires multiple passes at solving the diffusion equation in order to establish the field $\phi_0$ consistent with the current $\rho$. Whether the extra computational burden of the force evaluation in the present density-based real Langevin scheme is offset by avoidance of the sign problem remains to be seen and, indeed, may prove to be system and problem dependent.

Note that in a Monte Carlo implementation, the minor complications due to the positivity of $\rho(r)$ and the conservation of the integral $\int dr \rho(r)$ are easy to overcome. First, one discretizes space. To implement the conservation of the total number of monomers, one starts with a configuration of $\rho(r)$ that has the right number of monomers, and then one chooses randomly two lattice sites, say $r_1$ and $r_2$. The elementary Monte Carlo variation of $\rho(r)$ consists in modifying simultaneously $\rho$ at two points $r_1$ and $r_2$ according to $\rho(r_1) \to \rho(r_1) + \delta \rho$ and $\rho(r_2) \to \rho(r_2) - \delta \rho$. This procedure obviously conserves the total integral of $\rho(r)$ in space. Also, to enforce the positivity of $\rho(r)$, one just has to reject any variation of $\rho$ that produces a negative $\rho$.

### III. MORE COMPLICATED SYSTEMS

The concepts and methods presented above can be extended in a straightforward way to virtually any type of inhomogeneous polymer system. We illustrate in the context of a solution of AB diblock copolymers.

Let $f$ be the volume fraction of A monomers and $1 - f$ the volume fraction of B monomers on each diblock copolymer chain with a total of $N$ monomers. Denoting by $v_{AA}(r)$, $v_{BB}(r)$, and $v_{AB}(r)$ the respective potentials of mean force (mediated by the solvent) between the different species of monomers, and using the same notations as in the previous section, we
may write

\[ Z = \frac{1}{M!} \int \mathcal{D}\rho_A \mathcal{D}\rho_B \exp \left( -\frac{\beta}{2} \int drdr' \rho_A(r) v_{AA}(r-r') \rho_A(r') \right) \]
\[ \times \exp \left( -\frac{\beta}{2} \int drdr' \rho_B(r) v_{BB}(r-r') \rho_B(r') \right) \]
\[ \times \exp \left( -\beta \int drdr' \rho_A(r) v_{AB}(r-r') \rho_B(r') Z_A(\rho_A) Z_B(\rho_B) \right) \]  

where the functions \( Z_A(\rho_A) \) and \( Z_B(\rho_B) \) are defined by

\[ Z_A(\rho_A) = \int \prod_{k=1}^{M} Dr_k \exp \left( -\frac{3}{2a^2} \sum_{k=1}^{M} \int_{0}^{fN} ds \left( \frac{dr_k}{ds} \right)^2 \right) \]
\[ \times \prod_r \delta \left( \rho_A(r) - \sum_{k=1}^{M} \int_{0}^{fN} ds \delta(r-r_k(s)) \right) \]  

and

\[ Z_B(\rho_B) = \int \prod_{k=1}^{M} Dr_k \exp \left( -\frac{3}{2a^2} \sum_{k=1}^{M} \int_{fN}^{Nf} ds \left( \frac{dr_k}{ds} \right)^2 \right) \]
\[ \times \prod_r \delta \left( \rho_B(r) - \sum_{k=1}^{M} \int_{fN}^{Nf} ds \delta(r-r_k(s)) \right) \]  

It is clear from their definitions that both \( Z_A \) and \( Z_B \) are positive definite, and using a Fourier representation for the delta functionals, one can again show that in the limit of an infinite number of chains (with infinite volume and finite concentration), the corresponding “chemical potential” field integrals can be asymptotically evaluated by the saddle point method. The resulting expression for the entropy functional

\[ S(\rho_A, \rho_B) = \ln[Z_A(\rho_A)Z_B(\rho_B)] \]  

is

\[ S(\rho_A, \rho_B) = \int dr \left( i\phi_A \rho_A + i\phi_B \rho_B \right) + M \ln Q(i\phi_A, i\phi_B) \]  

where \( Q(i\phi_A, i\phi_B) = \int dr \Psi(r, N) \). The propagator \( \Psi(r, s) \) satisfies (again, subject to \( \Psi(r, 0) = 1 \))

\[ \left( \frac{\partial}{\partial s} - \frac{a^2}{6} \nabla^2 + w(r, s) \right)\Psi(r, s) = 0 \]  

where \( w(r, s) = i\phi_A(r) \) for \( s \in (0, Nf) \) and \( w(r, s) = i\phi_B(r) \) for \( s \in (Nf, N) \). The density fields are related to the saddle point chemical potentials, \( \phi_A \) and \( \phi_B \), by equations analogous to eq. \[10\]

\[ \rho_A(r) = \frac{M}{Q(i\phi_A, i\phi_B)} \int_{0}^{Nf} ds \Psi(r, s)\Psi^*(r, N-s) \]
\[ \rho_B(r) = \frac{M}{Q(i\phi_A, i\phi_B)} \int_{N_f}^N ds \, \Psi(r, s)\Psi^*(r, N - s) \]  

(46)

A second propagator \( \Psi^*(r, s) \) enters these expressions due to the head-to-tail asymmetry of diblock copolymers. It satisfies

\[ \left( \frac{\partial}{\partial s} - \frac{a^2}{6} \nabla^2 + w^*(r, s) \right) \Psi^*(r, s) = 0 \]  

(47)

subject to \( \Psi^*(r, 0) = 1 \), where \( w^*(r, s) = i\phi_B(r) \) for \( s \in (0, N(1 - f)) \) and \( w^*(r, s) = i\phi_A(r) \) for \( s \in (N(1 - f), N) \).

A formalism very similar to this was employed recently, without formal justification, for a real Langevin dynamics study of spinodal decomposition in binary polymer blends [24] and in studying microemulsion formation in ternary copolymer alloys [25]. The present analysis shows that this is indeed a rigorous approach to simulating fluctuating systems of macroscopic size.

IV. SUMMARY AND DISCUSSION

In the present paper we have examined statistical field theories of polymeric fluids with the objective of identifying field-based models that are well-suited to numerical simulation. It has been known for some time that essentially any microscopic (particle-based) model of a polymeric fluid can be converted to a field theory in density and chemical potential variables [8, 13], e.g. for a one-component system

\[ Z = \int \mathcal{D}\rho \int \mathcal{D}\phi \ \exp[-\mathcal{H}(\rho, \phi)] \]  

(48)

where the effective Hamiltonian \( \mathcal{H}(\rho, \phi) \) is a complex functional of the two fields. In the case of pair interactions among monomers, \( \mathcal{H}(\rho, \phi) \) is a quadratic form in \( \rho \), so the density field can be integrated out exactly (for potentials with an inverse) to obtain a statistical field theory in \( \phi \)

\[ Z = \int \mathcal{D}\phi \ \exp[-\mathcal{G}(\phi)] \]  

(49)

In this case, the effective Hamiltonian \( \mathcal{G}(\phi) \) is complex. This type of field theory has been studied using approximate analytical methods for many years [1] and has recently been examined with complex Langevin simulation techniques [6, 9, 18]. Unfortunately, the non-positive definite character of the Boltzmann factor \( \exp(-\mathcal{G}) \) gives the integrand an oscillatory
character ("sign problem"), which can dramatically hinder the convergence of numerical simulations.

Rather than transforming to a field theory in the single field $\phi$, a more typical strategy for studying inhomogeneous polymers is to invoke a mean-field approximation. This amounts to evaluating both integrals in eq. (48) at leading order by the saddle point method. This reproduces the familiar self-consistent field theory (SCFT) and amounts to

$$Z \approx \exp[-\mathcal{H}(\rho^*, \phi^*)]$$ (50)

where $\rho^*$ and $\phi^*$ are the "self-consistent" density and chemical potential fields that satisfy $\delta \mathcal{H}/\delta \rho^* = 0, \delta \mathcal{H}/\delta \phi^* = 0$. This is a powerful approach, but it neglects all field fluctuations, so the utility of the SCFT is limited to highly concentrated systems of high molecular weight polymers, far from critical points and phase transitions where soft fluctuation modes occur.

In the present paper, we have discussed a third approach in which the chemical potential field $\phi$ is integrated out of eq. (48), leading to a field theory solely in the monomer density

$$Z = \int \mathcal{D}\rho \, \exp[-H(\rho)]$$ (51)

This approach has the benefit of producing a real field theory in which $\exp(-H)$ is positive definite so that the sign problem is avoided and standard Monte Carlo and real Langevin simulation methods can be applied. In the past it was assumed that the $\phi$ integral necessary to reduce eq. (48) to eq. (51) was intractable, leading various authors to impose a variety of approximations in order to construct the density functional $H(\rho)$ [26, 27]. We have demonstrated here, however, that the $\phi$ integral in eq. (48) can be exactly evaluated by the saddle point method provided that the thermodynamic limit is taken. The resulting real energy functional $H(\rho)$ is given (for a homopolymer solution) by eq. (35) and involves the constrained (real) saddle point $i\phi_0(r)$, which is the mean chemical potential field required to generate a particular density pattern $\rho(r)$.

We believe that our discovery will have a number of significant implications. First of all, it provides theoretical justification for ad hoc approaches that have been used to include thermal fluctuations in density field-based simulations of polymers [24, 28]. Secondly, by circumventing the sign problem, it avoids the difficulties that have been encountered in field-theoretic polymer simulations based on eq. (49). Moreover, with a real field theory, a much wider variety of options exist for carrying out stochastic computer simulations. Finally, we
note that our proof that the $\phi$ integral in eq. (48) is dominated for large systems by the saddle point carries over to a much broader class of classical fluids, both simple and complex. For example, real density functionals can be constructed using the present methods for alternative polymer chain models, such as the worm-like chain used to describe semiflexible polymers. Real density-based field theories for a wide variety of polymers, copolymers, and alloys can be derived, including solutions of charged polyelectrolyte systems. In the case of simple fluids, we believe that the present formalism will provide new insights and numerical strategies for improving density functional methods, including the treatment of crystallization and melting.

A clear disadvantage of the density field approach, at least for polymers, is that force or energy evaluations require the computation of the mean-field $i\phi_0(r)$ from equations such as (10) at constrained monomer density $\rho(r)$. This must be done iteratively and each iteration requires an independent solution of the diffusion equation (11). In constrast, evaluation of the energy $\mathcal{G}(\phi)$ in the potential field formulation of eq. (19) requires only a single solution of the diffusion equation. Since the vast majority of the computational effort in a field-theoretic computer simulation of a polymeric fluid is spent in solving the diffusion equation, it is essential that a very efficient scheme be devised for computing $i\phi_0$ given $\rho$. We are cautiously optimistic, however, that the extra computational burden associated with simulating in the density variables will be more than offset by the avoidance of the sign problem.

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