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Free Energy Evaluation in Field-Theoretic Polymer Simulations

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We present a thermodynamic integration method for free energy evaluation in field-theoretic simulations of classical fluids and polymers. The approach employs an Einstein crystal reference state, analogous to a method developed for particle simulations of crystals by Frenkel and Ladd, but applies equally well in the present context to ordered and disordered phases. Thermodynamic averages are computed using complex Langevin sampling, which is effective against the sign problem inherent to polymer field theories. Our method is illustrated in the context of a diblock copolymer melt, where we provide a demonstration of the experimentally observed transition between the cubic gyroid and disordered phases.

The use of computer simulations to predict accurate phase diagrams relies upon resolving the free energy of competing phases near transitions. Simulations of classical particle-based models are well-adapted to such free energy calculations. For example, a number of techniques have been used in fluid state Monte Carlo and molecular dynamics simulations to determine both relative and absolute free energies. These include the methods of particle insertion [1], multiple histograms [2], and thermodynamic integration to a reference ideal gas or high temperature phase [3]. In solid phase calculations, applicable techniques include the single occupancy cell method [4], lattice switching [5], and thermodynamic integration to a low temperature or Einstein crystal reference [6].

Despite these advances for particle simulations, free energy evaluation methods have yet to be explored in the context of simulations of field theory models increasingly used to study mesoscale phenomena in complex fluids and polymers. Such *field-theoretic simulations (FTS)* are an attractive way to study the equilibrium properties of inhomogeneous polymers on scales ranging from nanometers to microns [7–9]. In the FTS technique, coarse-grained particle-based models of polymers are converted to statistical field theories through the introduction of Hubbard-Stratonovich auxiliary fields. The fields are given a finite representation (usually by collocating on a lattice) and simulations are performed by devising an appropriate stochastic procedure for importance sampling the discrete theory. A number of difficult problems in polymer physics have recently succumbed to this FTS approach, including the fluctuation-stabilization of polymeric bicontinuous microemulsions [10] and complexation phenomena in solutions of oppositely charged polyelectrolytes [11].

Heretofore, the free energy has only been accessible in a mean-field approximation in which fluctuations about mean (saddle point) field configurations are neglected. This approach, known as self-consistent field theory (SCFT), has been successfully used to investigate the phase behavior of many polymeric systems, most notably block copolymers [12]. However, the validity of the mean-field approximation is largely restricted to molten polymers of high molecular weight, and SCFT is inapplicable to broad classes of solvated and lower molecular weight systems [13]. Even in the context of polymer melts, the SCFT approach has limitations, especially near phase transitions where composition fluctuations can play an important role. This can be seen explicitly in Fig. 1, where SCFT fails qualitatively to describe the order-disorder transition of a diblock copolymer melt. In particular, the ordered $Ia\bar{3}d$ cubic "gyroid" phase (G) is observed in experiments to melt directly to the disordered phase (the Flory parameter χ is inversely proportional to temperature T) [14], whereas SCFT predicts that G transforms to two intermediate ordered phases before melting [15]. Capturing this type of behavior requires a quantitative treatment of field fluctuations that is beyond current analytical methods, but is accessible in full field-theoretic simulations. However, prior to this work, there was no strategy for accessing relative and absolute free energies of competing phases within FTS.

Here we show that the thermodynamic integration method of Frenkel and Ladd [6] can be adapted to compute absolute free energies in field-theoretic simulations. Key to this adaptation is an Einstein crystal reference state for the discrete field theory consisting of uncoupled harmonic oscillators placed at collocation points within the simula-
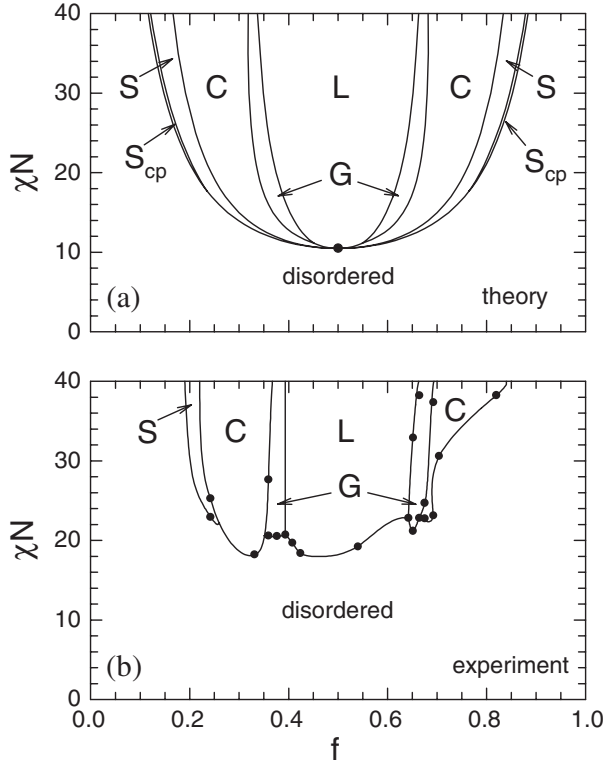
FIG. 1.   Mean-field (a) and experimental (b) phase diagrams
for an AB diblock copolymer melt in the coordinates of χN
(product of Flory χ parameter and total copolymer length N) and
the A block volume fraction f. Labeled phases are bcc spheres
(S), close-packed spheres (S_{cp}), hex cylinders (C), cubic gyroid
(G), and lamellae (L). Numerical SCFT was used to calculate the
mean-field phase diagram. The experimental results are for the
polystyrene-polyisoprene system [14]. Reproduced with permis-
sion from [15].

tion cell. Because the symmetry of the field collocation
lattice does not restrict the symmetries of the fluid and
solid phases that can be described by the theory, unlike the
original Frenkel-Ladd approach, our method is equally
applicable to disordered fluid phases and ordered meso-
phases. An alternative method based on the application of
an external ordering field was recently proposed by Müller
and Daoulas [16], although it has yet to be implemented in
the FTS context and is limited to the computation of
relative free energies between ordered and disordered
phases.

We describe our technique for an AB diblock copolymer
melt and adopt the notation of a recent book on the subject
(Model E in Ref. [9]). In the canonical ensemble of this
model, n incompressible AB diblock copolymers each of
length N reside in a system of volume V. Each chain is
modeled as a continuous Gaussian chain with a volume
fraction of A segments given by f, and the interactions
between the A and B segments are described by the Flory
parameter, χ. The partition function $Z(n, V, T)$ of this
model can be recast in field-theoretic form, $Z =$

$\int \mathcal{D}W_{\pm} \exp(-H[W_{\pm}])$, by introducing two auxiliary po-
tential fields, $W_{\pm}(\mathbf{x})$. The effective Hamiltonian is

$$H[W_{\pm}] = C \int d\mathbf{x} \left[\frac{W_-^2}{\chi N} - iW_+ \right] - C\tilde{V} \ln Q[W_{\pm}]. \quad (1)$$

Here, positions $\mathbf{x}$ have been expressed in units of the
unperturbed polymer radius-of-gyration $R_g \sim N^{1/2}$, and
the dimensionless system volume is $\tilde{V} = V/R_g^3$. The pa-
rameter $C = nR_g^3/V$ is a reduced polymer concentration,
and $Q[W_{\pm}]$ is the partition function of a *single* polymer
chain experiencing the fields $W_{\pm}(\mathbf{x})$. This object can be
computed deterministically by means of $Q[W_{\pm}] =$
$\tilde{V}^{-1} \int d\mathbf{x} q(\mathbf{x}, 1)$, where the propagator $q(\mathbf{x}, s)$ satisfies
the Feynmann-Kac equation $\partial_s q = \nabla^2 q - \psi q$ with
$q(\mathbf{x}, 0) = 1$, and ψ is a block-specific potential field given
by

$$\psi(\mathbf{x}, s) \equiv \begin{cases} iW_+(\mathbf{x}) - W_-(\mathbf{x}) & 0 < s \le f \\ iW_+(\mathbf{x}) + W_-(\mathbf{x}) & f < s < 1 \end{cases}. \quad (2)$$

Both the energy functional H and statistical weight
$\exp(-H)$ of the field theory are complex.

As described above, polymer field theories can be simu-
lated in either the mean-field approximation (SCFT) or by
importance sampling the full partition function (FTS). The
SCFT approach assumes that Z is dominated by a single set
of field configurations $W_{\pm}^*(\mathbf{x})$, which satisfy the saddle
point equations $\delta H/\delta W_{\pm}(\mathbf{x}) = 0$. In the above model,
the SCFT free energy $H[W_{\pm}^*]$ is asymptotically exact for
$C \sim N^{1/2} \to \infty$, but is a poor approximation to the exact
free energy $F = -\ln Z$ outside of this limiting regime. In
these cases, an FTS approach can be employed with a
sampling technique suitable for complex weights. One
such method, complex Langevin (CL) sampling [17,18],
has been shown to be particularly effective in FTS studies
of polymers [7,9]. The CL method involves generating a
stationary Markov chain of *complex* field configurations
(used to compute equilibrium averages) by numerical in-
tegration of the following fictitious stochastic dynamics

$$\frac{\partial W_{\pm}(\mathbf{x}, t)}{\partial t} = -\frac{\delta H[W_{\pm}]}{\delta W_{\pm}(\mathbf{x}, t)} + \eta(\mathbf{x}, t), \quad (3)$$

where $\eta(\mathbf{x}, t)$ is a *real*, Gaussian white noise with the
average properties $\langle \eta(\mathbf{x}, t) \rangle = 0$ and $\langle \eta(\mathbf{x}, t)\eta(\mathbf{x}', t') \rangle =$
$2\delta(\mathbf{x} - \mathbf{x}')\delta(t - t')$. We note that advanced algorithms
are needed for stochastic integration of the CL equations
to ensure stability and accuracy [19].

In adapting the Frenkel-Ladd [6] approach to a field-
based simulation, we require an appropriate Einstein crys-
tal reference state. This can be described in the continuum
field theory by a reference Hamiltonian $H_{\text{ref}} =$
$H^* + \int d\mathbf{x}[\alpha_+(\Delta W_+)^2 + \alpha_-(\Delta W_-)^2]$, where $H^* =$
$H[W_{\pm}^*]$ is the mean-field free energy corresponding to a
mean-field solution $W_{\pm}^*$, $\alpha_i > 0$ are real "spring con-
stants," and $\Delta W_i(\mathbf{x}) \equiv W_i(\mathbf{x}) - W_i^*(\mathbf{x})$. In the correspond-

ing discrete field theory used in numerical simulations, the $W_\pm(\mathbf{x})$ fields are replaced by two M-vectors of field values $(W_{\pm,j}, \; j = 1, \ldots, M)$ on an M-site collocation grid of uniform spacing Δx. The reference state of the discrete model is thus $H_{\mathrm{ref}} = H^* + (\Delta x)^3 \sum_i \sum_j \alpha_i (\Delta W_{i,j})^2$ and describes a harmonic crystal of $2M$ uncoupled oscillators. The absolute free energy of this state, F_{ref}, can be determined analytically by evaluating $2M$ uncoupled Gaussian integrals for each $W_{\pm,j}$ degree of freedom.

This reference state can be applied in FTS-CL simulations by defining a new Hamiltonian $\tilde{H}$ that depends linearly on a coupling parameter $\Lambda \in [0, 1]$,

$$\tilde{H}[W_\pm, \Lambda] = (1 - \Lambda)H[W_\pm] + \Lambda H_{\mathrm{ref}}[W_\pm]. \qquad (4)$$

At $\Lambda = 1$, the system is fully harmonic and has the reference free energy $F_{\Lambda=1} = F_{\mathrm{ref}}$. In the other limit of $\Lambda = 0$, $\tilde{H}$ reduces to the Hamiltonian H of the fully interacting field theory. FTS-CL simulations of the extended model with statistical weight $\exp(-\tilde{H})$ can be carried out by simply replacing the force term in Eq. (3) with $\delta\tilde{H}/\delta W_\pm$. CL-computed averages over field configurations using this extended statistical weight at prescribed Λ are denoted by $\langle \ldots \rangle_\Lambda$. The absolute free energy of the original field theory can be obtained by a simple thermodynamic integration between the $\Lambda = 0$ and 1 states,

$$F = F_{\Lambda=0} = F_{\mathrm{ref}} - \int_0^1 d\Lambda \left\langle \frac{\partial \tilde{H}[\Lambda, W_\pm]}{\partial \Lambda} \right\rangle_\Lambda. \qquad (5)$$

Once the free energy of a single point in the parameter space of the model has been determined, other thermodynamic integration paths can be followed to map the entire free energy landscape.

A few practical matters remain to be described. Firstly, the phase can be controlled by selecting among multiple solutions of the SCFT equations. Numerical mean-field solutions $W_\pm^*(\mathbf{x})$ possessing the symmetries of all competing phases in the phase diagram can be inexpensively generated [9,15]. By pinning the harmonic reference state to the saddle point for a phase that is stable or metastable in the $\Lambda = 0$ state, the targeted phase will usually be preserved in simulation trajectories conducted along the Λ integration path. Secondly, optimal values of the spring constants α_i [i.e., values that make the integrand of Eq. (5) slowly varying in Λ] can be obtained by a preliminary simulation of the $\Lambda = 0$ model to assess the mean-squared strength of field fluctuations [6]. Finally, most polymer field theory models have ultraviolet divergences that reflect a sensitivity of CL-derived averages to the lattice spacing Δx. Thus, while our method yields absolute free energies of phases of the discrete field theory, the values can change rapidly upon lattice refinement. We have found that these spurious contributions are readily extracted by regularizing the free energies with that of a common phase (e.g., a disordered fluid phase) simulated on the *same* lattice. Such regularized free energies converge smoothly to finite

values upon decreasing Δx. For details, see Fig. 1 in the supplementary information [20].

To demonstrate the technique, we have chosen to investigate the effect of including fluctuations on the phase diagram for an AB diblock copolymer melt. In the mean-field limit of $C \to \infty$, the phase diagram [Fig. 1(a)] can be completely characterized by two parameters: χN and f [12,21]. However, as C is reduced to values typical in experiment (10–100), fluctuation corrections to the mean-field diagram become significant [22]. In Fig. 2 we present the shift of the order-disorder transition (ODT) of a diblock copolymer melt with $C = 50$. The simulations were conducted in periodic cells using plane-wave-based spectral collocation methods and a semi-implicit stochastic integration of the CL equations [19]. In this preliminary study, the simulation cell for each ordered phase was chosen as one stress-free parallelepiped unit cell obtained from SCFT. The disordered phase was simulated using multiple cells of identical size and shape to the counterpart ordered phase along the order-disorder boundary. This procedure allowed for optimal cancellation of ultraviolet divergences. While a comprehensive finite-size analysis was not conducted, we confirmed at three different f values that use of larger simulation cells containing 2^3 unit cells of the ordered phases produced insignificant changes in the computed ODT.

The phase boundaries were determined by first calculating F for a given phase by a Λ integration at a reference χN [by means of Eq. (5)], then integrating along a second trajectory in $1/(\chi N)$ while holding C and f fixed. The phase transitions were located by the condition $F_{\mathrm{ord}} = F_{\mathrm{dis}}$. For select values of f, these phase boundaries were verified by a direct calculation of F using only a Λ integration from a mean-field metastable disordered phase. Examples of locating the L-D and G-D transitions and a
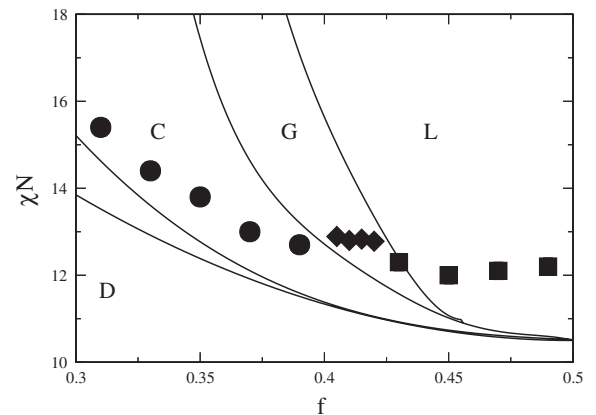

FIG. 2. Comparison of the mean-field (curves) and FTS-CL simulated (symbols) order-disorder boundaries for a diblock copolymer melt at $C = 50$. The symbols denote boundaries between the disordered phase (D) and the C (circles), G (diamonds), and L (squares) mesophases.

description of parameters and methods used in the simulations are provided in the supplementary information [20].

The estimated errors are within the size of the symbols, although we did not conduct a comprehensive finite-size analysis which would involve simulations of large systems with multiple unit cells of the L, G, and C mesophases [20]. As in the experimental phase diagram of Fig. 1(b), and unlike the SCFT diagram, the L, G, and C phases are predicted to melt directly into the disordered phase and the phase envelope has been shifted to higher values of χN. Similar results were obtained previously using a large C asymptotic Hartree analysis for weakly asymmetric diblocks [22] as well as the $Ia\bar{3}d$ [23] and $Fddd$ [24] phases. This shift has also been studied using lattice-based Monte Carlo simulations [25]. However, the present method is not restricted to either weak fluctuations or diblock asymmetry (large C or $|f - 1/2| \ll 1$). When put in the context of Fredrickson-Helfand theory [22], the simulations here show a larger shift in the ODT than predicted around $f = 0.5$. This disagreement may stem from the approximations made in the Hartree analysis. Indeed, the present study is not limited to field fluctuations about the leading harmonics of the saddle-point solution.

An attractive feature of our thermodynamic integration method is its general applicability to a wide range of polymeric fluids of arbitrary complexity. Moreover, the technique allows for quantitative investigations of phase transitions without the need to simulate the transition itself—hence avoiding long simulation times and hysteretic effects. The method also avoids the use of order parameters, suitable choices of which are often difficult to identify and expensive to compute.

On the downside, free energy estimation with the technique requires intensive numerical simulations that are subject to several potential sources of error, most notably statistical sampling and finite-size effects. We have seen that ultraviolet divergences can be approximately canceled by use of appropriate reference simulations on the same lattice, but much more remains to be understood about how to properly deal with these singularities in a numerical context as the continuum limit is approached.

In summary, we have developed a thermodynamic integration method for determining absolute and relative free energies of arbitrary phases in field-based simulations. While generally applicable to classical fluid models, the technique should be most valuable in the study of mesostructured polymeric fluids. Beyond the diblock copolymer melt examined here, we expect that the method will aid the development of accurate phase diagrams for systems ranging from complex block copolymers and polymer blends to multicomponent polymer solutions, liquid crystalline polymers, and polyelectrolytes.

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