Polymer Field Theory for Multimonomer Incompressible Models: Symmetric Formulation and ABC Systems

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Abstract

We present a symmetric formulation of polymer field theory for incompressible systems containing any number M of monomer types, in which all monomers are treated on an equal footing. This is proposed as an alternative to the multi-species exchange formulation, which imposes incompressibility by eliminating one monomer type. The symmetric formulation is shown to correspond to the incompressible limit of a corresponding compressible model, and to reduce in the case $M = 2$ to the usual formulation of field theory for incompressible AB systems. An analysis of ABC systems ($M = 3$) identifies ranges of interaction parameter values in which a fully fluctuating field theory requires one, two or three imaginary-valued fields. ABC systems with parameters that satisfy the Hildebrand solubility parameter approximation are shown to require only one imaginary pressure-like field, much like AB systems. Generalization of the partial saddle-point approximation to $M > 2$ is discussed.

Introduction

Stochastic field theoretic simulation (FTS) methods have matured over the past 20 years into powerful tools for studying heterogeneous polymer materials.[1–12] Such methods are based on a transformation of an underlying particle-based model into a functional integral over a set of monomer chemical potential fields. The simplest field theoretic approach, self-consistent field theory (SCFT), identifies a single field configuration that is a saddle-point of a corresponding field theoretic Hamiltonian functional. Stochastic FTS methods go beyond SCFT by randomly sampling a statistical ensemble in which each possible field configuration is assigned a weight that is determined by the value of this Hamiltonian. Existing FTS methods can be primarily divided into fully fluctuating (FF) methods, which are equivalent to a corresponding particle-based model, and methods that rely a partial saddle-point (PS) approximation, which improve computational efficiency at some cost in accuracy.

Most prior FTS studies of block copolymers and polymer mixtures have focused on systems with only two types of monomer, which we refer to as AB systems. In the standard formulation of field theory for such systems, chemical potentials associated with species A and B are expressed in terms of a pressure-like field W_+ and and an exchange field W_-.[3,11] The resulting fully fluctuating formulation of the partition function as a functional integral for an AB system with a positive Flory Huggins parameter $\chi > 0$ requires that contributions to these monomer chemical potentials arising from W_+ be imaginary, while those arising from W_- be real. In a partial saddle-point approximation for an AB system, W_+ is approximated by its value at a partial saddle-point. This is equivalent to the use of a self-consistent field approximation to treat the incompressibility constraint. The partial saddle-point approximation yields a theory in which the monomer chemical fields and the Hamiltonian are real, thereby allowing the use of conventional Monte-Carlo and Brownian dynamics sampling methods. In what follows, we will sometimes refer to fully fluctuating simulation methods as FF-FTS methods, and those that rely on a partial saddle-point approximation as PS-FTS methods. Studies of AB systems with PS-FTS methods by Matsen and coworkers have

shown an encouraging balance between accuracy and computational expense,[8–12] making PS-FTS an attractive intermediate alternative to SCFT and FF-FTS.

Many properties of complex polymer materials are adequately described by coarse-grained models that treat these materials as incompressible. When this approximation is appropriate, its validity is the result of a disparity in real materials between the large free energy penalties for changes in total monomer density (characterized by a bulk modulus) and much smaller penalties for changes in composition at fixed density (often characterized by Flory-Huggins interaction pararatmers). Most SCFT studies have relied on an incompressible model. Different FTS methods differ in their treatment of compression. Most FF-FTS studies have used complex Langevin (CL) sampling to study compressible models with a "smeared" (i.e., nonlocal) interaction between monomers.[6,7] This choice is motivated primarily by computational considerations, because compressibility and nonlocal interactions are both found to alleviate numerical instabilities that would otherwise plague CL simulations. The use of an incompressible model thus appears, as a practical matter, to be incompatible with complex Langevin sampling. Studies that use PS-FTS methods have, however, generally been based on an incompressible model of AB systems with local interactions that is closely analogous to the standard incompressible model of SCFT.[8–12] The formulation of a fully fluctuating field theory for incompressible models given here is thus intended primarily as a starting point for PS-FTS studies of systems with $M > 2$, where M denotes the number of monomer types.

The only existing formulation of polymer field theory that was designed explicitly for incompressible systems with $M > 2$ is the multi-species exchange (MSE) formulation of Düchs, Delaney and Fredrickson.[5] In this formulation, incompressibility is imposed by expressing the concentration of one type of monomer as a function of the other $M-1$ monomer concentrations, thus explicitly eliminating one monomer type. The MSE formulation requires an arbitrary choice of which monomer type to eliminate, and yields working equations whose forms reflect this choice, though all final results for observable quantities are independent of

this choice.[5] (Throughout this work, we refer to monomer "types", rather than "species", but retain the name of the MSE formulation chosen by its authors, in which the word species refer to what we call a monomer type).

Section 2 of this article presents a "symmetric" formulation of incompressible field theory for $M \geq 2$ that treats all monomer types on an equal basis, which we propose as an alternative to the MSE formulation. This symmetric formulation is based on the introduction of a so-called projected χ matrix. This quantity, denoted here by $\tilde{\boldsymbol{\chi}}$, is defined by an orthogonal projection of the full $M \times M$ matrix of Flory-Huggins χ parameters into the $M-1$ dimensional subspace associated with composition fluctuations at fixed total monomer concentration. The result of this projection is a singular $M \times M$ symmetric matrix of rank $M-1$ that has $M-1$ eigenvectors with generally nonzero eigenvalues, and a null space spanned by vector that is associated with changes in total monomer concentration (i.e., compression). In the symmetric formulation of fully fluctuating polymer field theory, negative eigenvalues of $\tilde{\boldsymbol{\chi}}$ are associated with real-valued chemical potential field components (i.e., components that yield real contributions to the fields associated with specific monomer types), while positive and vanishing eigenvalues are associated with imaginary components. We show in section 3 that the usual treatment of incompressible AB systems is recovered as a special case of the symmetric formulation. We also show in section 6 how the symmetric formulation can be obtained by taking the incompressible (infinite compression modulus) limit of an analogous compressible model.

Section 4 of this paper discusses ABC systems, with $M = 3$. A general analysis of such systems gives criterion for ranges of values of the interaction parameters for which $\tilde{\boldsymbol{\chi}}$ has different possible number of negative eigenvalues, corresponding to different number of real- or imaginary-valued field components. We also consider a restricted model in which the χ parameters are assumed to obey the Hildebrand solubility parameter approximation, which is a useful but approximate guide to the behavior of simple non-polar mixtures. We show that this approximation leads to a set of interaction parameters for which one of the two

nontrivial eigenvalue exactly vanishes, causing fluctuations of the auxiliary field associated with this eigenvalue to be completely suppressed as a result. The result is a formulation for this class of ABC systems that is closely analogous to the standard formulation for AB systems, with one real-valued field and on imaginary pressure-like field.

Section 5 proposes a generalization of the partial saddle-point approximation to systems with $M > 2$, and discusses the expected accuracy of the resulting approximation.

The present work was motivated by the fact that all of its authors are involved in the development of open-source software packages that provide both SCFT and PS-FTS methods for polymer liquids. Two authors (D.C.M and K.C) contribute to the PSCF package[13,14] in which PS-FTS methods are currently being implemented. The third (D.Y.) is the primary developer of a newer package that enables use of machine-learning methods to accelerate identification of the partial-saddle point in PS-FTS methods.[15] This work was thus motivated for all of us by an interest in extending PS-FTS methods to systems with $M > 2$, and the desire for a more convenient and elegant mathematical formalism around which to design algorithms and software. Among other purposes, this work is thus intended to explain and document the theory underlying the PS-FTS algorithms that are used or planned for use in both of these software packages.

Incompressible Field Theory

Consider a mixture of polymers and solvents containing M types of monomer. Let $c_i(\mathbf{r})$ denote the concentration of monomers of type i at point $\mathbf{r}$ within the mixture in a specific mechanical microstate (i.e., a specific list of monomer positions). We focus here on incompressible models in which the sum of the monomer concentration must satisfy a constraint requiring that

$$\sum_{i=1}^{M} c_i(\mathbf{r}) = c_0 \tag{1}$$

for all $\mathbf{r}$, in which c_0 is the prescribed constant total monomer concentration. Let $v = 1/c_0$ denote the corresponding monomer volume.

Consider a model with a potential energy (excluding any penalty added to enforce the above constraint) of the form

$$U = U_{\rm id} + U_{\rm int} + U_{\rm ext} \quad , \tag{2}$$

in which $U_{\rm id}$ is the intramolecular potential energy of a gas of non-interacting molecules, and

$$\begin{aligned} U_{\rm int} &= \frac{v}{2} \int d\mathbf{r}\ \chi_{ij} c_i(\mathbf{r}) c_j(\mathbf{r}) \\ U_{\rm ext} &= -\int d\mathbf{r}\ y_i(\mathbf{r}) c_i(\mathbf{r}) \quad . \end{aligned} \tag{3}$$

Here, χ_{ij} is an element of a symmetric matrix of dimensionless Flory-Huggins interaction parameters, while $y_1(\mathbf{r}), \ldots, y_M(\mathbf{r})$ are external "source" fields. Here and hereafter, we use an Einstein convention for summations over repeated indices i or j that represent monomer type indices, which are sums from $1, \ldots, M$. The external source fields can be used either to represent real physical effects, such as the effect of a confinement potential, or as formal devices to allow derivation of expressions for correlation functions via functional differentiation.

The partition function Z for such a fluid may be expressed to within an irrelevant multiplicative constant as a configurational integral

$$Z = \int \mathcal{D}\mathbf{r}\ e^{-U_{\rm id} - U_{\rm int} - U_{\rm ext}}\ \delta\left(\sum_{i=1}^{M} c_i(\mathbf{r}) - c_0 \right) \tag{4}$$

in which a δ-functional imposes the incompressibility constraint.

Orthogonal Projection

Let $\mathbf{c}(\mathbf{r})$ denote M component column vector with elements given by the monomer concentrations $c_1(\mathbf{r}), \ldots, c_M(\mathbf{r})$ at position $\mathbf{r}$. Let $\mathbf{e}$ denote a M component column vector

$$\mathbf{e} = \begin{bmatrix} 1 \\ 1 \\ \vdots \\ 1 \end{bmatrix} \tag{5}$$

with equal components $e_i = 1$ for all $i = 1, \cdots, M$. In this notation, the incompressibility constraint requires that

$$\mathbf{e}^T \mathbf{c}(\mathbf{r}) = c_0 \quad , \tag{6}$$

for all $\mathbf{r}$.

The symmetric formulation of polymer field theory considered here is based on a decomposition of $\mathbf{c}(\mathbf{r})$ and other vectors into components parallel and orthogonal to $\mathbf{e}$. To describe this, we define the $M \times M$ orthogonal projection matrices

$$\mathbf{Q} = \frac{1}{M}\mathbf{e}\mathbf{e}^T \qquad , \qquad \mathbf{P} = \mathbf{I} - \mathbf{Q} \quad , \tag{7}$$

where $\mathbf{I}$ is the $M \times M$ identity matrix. Note that $\mathbf{Q}\mathbf{e} = \mathbf{e}$ and $\mathbf{P}\mathbf{e} = 0$, and that $\mathbf{Q}$ and $\mathbf{P}$ are both symmetric. Multiplying a column vector by $\mathbf{Q}$ yields the orthogonal projection onto $\mathbf{e}$, while multiplying by $\mathbf{P}$ yields the projection into the $M-1$ dimensional subspace orthogonal to $\mathbf{e}$.

Let $\tilde{\mathbf{c}}(\mathbf{r})$ denote the orthogonal projection of $\mathbf{c}(\mathbf{r})$ into the subspace orthogonal to $\mathbf{e}$, given by

$$\tilde{\mathbf{c}}(\mathbf{r}) \equiv \mathbf{P}\mathbf{c}(\mathbf{r}) \quad . \tag{8}$$

By construction, $\mathbf{e}^T\tilde{\mathbf{c}}(\mathbf{r}) = 0$ for all $\mathbf{r}$, because $\mathbf{e}^T\mathbf{P} = 0$. Multipling $\mathbf{c}$ by $\mathbf{I} = \mathbf{P} + \mathbf{Q}$ yields

the decomposition

$$\mathbf{c}(\mathbf{r}) = \tilde{\mathbf{c}}(\mathbf{r}) + \frac{1}{M} c_0 \, \mathbf{e} \tag{9}$$

for states that satisfy the constraint requiring that $\mathbf{e}^T \mathbf{c}(\mathbf{r}) = c_0$.

Let $\tilde{\boldsymbol{\chi}}$ denote an $M \times M$ symmetric matrix defined by the matrix product

$$\tilde{\boldsymbol{\chi}} \equiv \mathbf{P} \boldsymbol{\chi} \mathbf{P} \quad , \quad , \tag{10}$$

which we refer to as the projected χ matrix. Let $\tilde{\chi}_{ij}$ denote element ij of matrix $\tilde{\boldsymbol{\chi}}$. By construction, the vector $\mathbf{e}$ is always an eigenvector of $\tilde{\boldsymbol{\chi}}$ with a zero eigenvalue, since $\mathbf{P}\mathbf{e} = 0$, implying that $\tilde{\boldsymbol{\chi}}$ is a singular matrix.

By substituting Eq. (9) for $c_i(\mathbf{r})$ into Eq. (3) for $U_{\rm int}$, while setting $C_M(\mathbf{r}) = c_0$, we obtain an expression for $U_{\rm int}$ as a sum of the form

$$U_{\rm int} = U_{\rm int}^{(2)} + U_{\rm int}^{(1)} + U_{\rm int}^{(0)} \tag{11}$$

in which

$$\begin{aligned} U_{\rm int}^{(2)} &= \frac{v}{2} \int d\mathbf{r} \; \tilde{\chi}_{ij} \tilde{c}_i(\mathbf{r}) \tilde{c}_j(\mathbf{r}) \\ U_{\rm int}^{(1)} &= \int d\mathbf{r} \; s_i \tilde{c}_i(\mathbf{r}) \\ U_{\rm int}^{(0)} &= S_M c_0 V/2 \quad , \end{aligned} \tag{12}$$

using Einstein notation for summations, where we have defined a vector

$$\mathbf{s} \equiv \boldsymbol{\chi} \mathbf{e}/M \tag{13}$$

with components $s_i \equiv \chi_{ij} e_j / M$ for all $i = 1, \ldots, M$, and a scalar

$$S_M \equiv \mathbf{e}^T \mathbf{s}/M = \mathbf{e}^T \boldsymbol{\chi} \mathbf{e}/M^2 \quad . \tag{14}$$

The use of the symbol S_M for the quantity defined in Eq. (14) is chosen for consistency with a convention for vector components that is introduced below.

Eigenvector Decomposition

A diagonal representation of $U_{\rm int}^{(2)}$ may be created by expanding $\mathbf{c}(\mathbf{r})$ in the a basis of eigenvectors of the projected χ matrix, $\tilde{\boldsymbol{\chi}}$. Let $\mathbf{v}_1, \ldots, \mathbf{v}_M$ denote M independent eigenvectors of $\tilde{\boldsymbol{\chi}}$, and let $\lambda_1, \ldots, \lambda_M$ be corresponding eigenvalues, such that

$$\tilde{\boldsymbol{\chi}} \mathbf{v}_\alpha = \lambda_\alpha \mathbf{v}_\alpha \tag{15}$$

for all $\alpha = 1, \ldots, M$. As already noted, $\mathbf{e}$ is always an eigenvector with a zero eigenvalue. By convention, we $\mathbf{e}$ to be the last eigenvector, defining

$$\mathbf{v}_M = \mathbf{e} \quad , \tag{16}$$

so that $\lambda_M = 0$. Because $\tilde{\boldsymbol{\chi}}$ is symmetric, it eigenvalues $\lambda_1, \ldots, \lambda_M$ are real, and we may take $\mathbf{v}_1, \ldots, \mathbf{v}_M$ to be real and orthogonal. The eigenvectors $\mathbf{v}_1, \ldots, \mathbf{v}_{M-1}$ thus span the $M-1$ dimensional subspace orthogonal to $\mathbf{e} = \mathbf{v}_M$. We choose a normalization in which

$$\mathbf{v}_\alpha^T \mathbf{v}_\beta = \delta_{\alpha\beta} M \tag{17}$$

for all $\alpha, \beta = 1, \ldots, M$. Note that this choice is compatible with the normalization of $\mathbf{e} = \mathbf{v}_M$, for which $\mathbf{e}^T \mathbf{e} = M$.

Let $C_\alpha(\mathbf{r})$ denote a component of concentration in a basis of these eigenvectors, given by

$$C_\alpha(\mathbf{r}) = \mathbf{v}_\alpha^T \mathbf{c}(\mathbf{r}) \tag{18}$$

for any $\alpha = 1, \ldots, M$. Note that, because $\mathbf{v}_M = \mathbf{e}$, the incompressibility of Eq. (6) requires

that $C_M(\mathbf{r}) = c_0$. We may expand $\tilde{c}_i(\mathbf{r})$ in a basis of the first $M-1$ eigenvectors as a sum

$$\tilde{c}_i(\mathbf{r}) = \frac{1}{M}\sum_{\alpha=1}^{M-1} C_\alpha(\mathbf{r}) v_{\alpha i} \quad , \tag{19}$$

or express $c_i(\mathbf{r})$ as a corresponding sum that includes an additional term with $\alpha = M$. Using these expansions of $\tilde{\mathbf{c}}$ and $\mathbf{c}$, we obtain

$$\begin{aligned} U_{\rm int}^{(2)} &= \frac{v}{2M}\sum_{\alpha=1}^{M-1}\int d\mathbf{r}\ \lambda_\alpha C_\alpha^2(\mathbf{r}) \\ U_{\rm int}^{(1)} &= \sum_{\alpha=1}^{M-1}\int d\mathbf{r}\ S_\alpha C_\alpha(\mathbf{r}) \\ U_{\rm ext} &= -\sum_{\alpha=1}^{M} Y_\alpha(\mathbf{r}) C_\alpha(\mathbf{r}) \quad , \end{aligned} \tag{20}$$

where we have defined components

$$S_\alpha \equiv \frac{1}{M}\mathbf{v}_\alpha^T \mathbf{s} \qquad Y_\alpha(\mathbf{r}) \equiv \frac{1}{M}\mathbf{v}_\alpha^T \mathbf{y}(\mathbf{r}) \tag{21}$$

for all $\alpha = 1, \ldots, M$, where $\mathbf{y}(\mathbf{r}) = [y_1(\mathbf{r}), \ldots, y_M(\mathbf{r})]^T$. Here and hereafter, we use lower case Greek letters α or β for eigenvector indices and small Latin letters $i, j, \ldots$ for monomer type indices, while using the Einstein summation convention and/or matrix multiplication only to represent sums over repeated monomer type indices. Note that, because $\mathbf{v}_M \equiv \mathbf{e}$, Eq. (21) yields a definition of the last element, S_M, that is identical to that given in Eq. (14).

Field components associated with positive or negative eigenvalues of $\tilde{\boldsymbol{\chi}}$ must be treated differently when constructing a functional integral representation of Z. Let L denote the number of negative eigenvalues of $\tilde{\boldsymbol{\chi}}$. By convention, for systems with $0 < L < M-1$, we take the first L eigenvalues $\lambda_1, \ldots, \lambda_L$ to be negative and take eigenvalues $L+1, \ldots, M-1$

to be non-negative, while $\lambda_M = 0$. For each $\alpha = 1, \ldots, M$, let

$$\lambda_\alpha = -\sigma_\alpha^2 |\lambda_\alpha| \quad , \tag{22}$$

with $\sigma_\alpha = 1$ for $\alpha = 1, \ldots, L$ (or $\lambda_\alpha < 0$) and $\sigma_\alpha = i$ for $\alpha = L+1, \ldots, M-1$. By convention, we also define $\sigma_M = i$.

Functional Integrals

A field-theoretic representation of Z may be obtained by using a Hubbard-Stratonovich transformation[3] to express the Boltzmann factor $\exp(-U_{\rm int}^{(2)})$ as a functional integral over $M-1$ auxiliary fields $\omega_1(\mathbf{r}), \ldots, \omega_{M-1}(\mathbf{r})$, of the form

$$\begin{aligned} e^{-U_{\rm int}^{(2)}} &= \frac{1}{N} \int \mathcal{D}\omega' \\ &\times \exp\left\{ -\sum_{\alpha=1}^{M-1} \int d\mathbf{r} \ \left[\frac{M\omega_\alpha^2}{2v|\lambda_\alpha|} + \sigma_\alpha \omega_\alpha C_\alpha \right] \right\} \ , \end{aligned} \tag{23}$$

where $\int \mathcal{D}\omega'$ denotes a functional integral over the fields $\omega_1, \ldots, \omega_{M-1}$, and where

$$N \equiv \int \mathcal{D}\omega' \exp\left\{ -\sum_{\alpha=1}^{M-1} \int d\mathbf{r} \ \frac{M\omega_\alpha^2}{2v|\lambda_\alpha|} \right\} \tag{24}$$

is a constant.

The δ-functional that constrains the total monomer concentration $C_M(\mathbf{r})$ may also be expressed as a functional integral

$$\delta(C_M(\mathbf{r}) - c_0) = \int \mathcal{D}\omega_M \exp\left\{ -i \int d\mathbf{r} \ \omega_M [\ C_M - c_0\ ] \right\} \tag{25}$$

in which $\omega_M(\mathbf{r})$ is a fluctuating Lagrange multplier field that imposes the constraint requiring that $C_M(\mathbf{r}) = c_0$, for all $\mathbf{r}$, and $\int \mathcal{D}\omega_M$ is a functional integral over this field.

Combining Eq. (23) with Eq. (25) for the δ-function constraint, while using the defini-

tions of $\Omega_1, \ldots, \Omega_M$, we obtain a partition function

$$Z = N^{-1} \int \mathcal{D}\omega \; e^{-H_{\rm f}} \int \mathcal{D}\mathbf{r} \; e^{-U_{\rm id} - H_{\rm c}} \quad , \tag{26}$$

in which $\int \mathcal{D}\omega$ denotes an integral over all M real fields $\omega_1, \ldots, \omega_M$,

$$H_{\rm f} = \int d\mathbf{r} \left\{ - \sum_{\alpha=1}^{M-1} \frac{M\Omega_\alpha^2}{2v\lambda_\alpha} - \Omega_M c_0 \right\} + U_{\rm int}^{(0)} \tag{27}$$

$$H_{\rm c} = \sum_{\alpha=1}^{M} \int d\mathbf{r} \; W_\alpha(\mathbf{r}) C_\alpha(\mathbf{r}) \quad . \tag{28}$$

Here, we have defined Wick rotated fields

$$\Omega_\alpha(\mathbf{r}) \equiv \sigma_\alpha \omega_\alpha(\mathbf{r}) \tag{29}$$

for all $\alpha = 1, \ldots, M$, with $\sigma_M = i$, and fields $W_1, \ldots, W_M$ that are given by

$$W_\alpha(\mathbf{r}) \equiv \Omega_\alpha(\mathbf{r}) + S_\alpha - Y_\alpha(\mathbf{r}) \tag{30}$$

for $\alpha = 1, \ldots, M-1$ and

$$W_M(\mathbf{r}) \equiv \Omega_M(\mathbf{r}) - Y_M(\mathbf{r}) \quad , \tag{31}$$

for $\alpha = M$. Hamiltonian component $H_{\rm f}$ depends only on the auxiliary fields (so that the subscript f denotes "field"), while component $H_{\rm c}$ introduces a coupling between auxiliary fields and the monomer concentrations (so that c denotes "concentration" or "coupling").

Let $w_1(\mathbf{r}), \ldots w_M(\mathbf{r})$ denote monomer chemical potential fields given by

$$w_i(\mathbf{r}) = \sum_{\alpha=1}^{M} W_\alpha(\mathbf{r}) v_{\alpha i} \qquad W_\alpha(\mathbf{r}) = \frac{1}{M} \sum_{j=1}^{M} v_{\alpha j} w_j(\mathbf{r}) \tag{32}$$

for all $i = 1, \ldots, M$ and $\alpha = 1, \ldots, M$. Using this definition, $H_{\rm c}$ can also be expressed as a

sum

$$H_{\rm c} = \sum_{i=1}^{M} \int d\mathbf{r}\; w_i(\mathbf{r}) c_i(\mathbf{r}) \quad . \tag{33}$$

The fields $w_1, \ldots, w_M$ are the monomer chemical potential fields used within the solution of modified diffusion equation to compute single-polymer partition functions.

The functional integral for the canonical partition function Z may be expressed as an integral

$$Z = N^{-1} \int \mathcal{D}\omega\; e^{-H[\omega]} \tag{34}$$

in which

$$H = H_{\rm f} - \ln Z_{\rm id} \tag{35}$$

is an effective Hamiltonian, and

$$Z_{\rm id}[w] = \int \mathcal{D}\mathbf{r}\; e^{-U_{\rm id} - H_{\rm c}} \tag{36}$$

is the partition function of a hypothetical gas of non-interacting molecules in which monomers of type i are subjected to a field $w_i(\mathbf{r})$.

In what follows, we use the notation $\langle \cdots \rangle_{\rm id}$ to denote averages over particle positions evaluated for a hypothetical ideal gas subjected to an external potential $H_{\rm c}$, as in the definition of $Z_{\rm id}$. We define average volume fraction fields as

$$\phi_i(\mathbf{r}) \;=\; v \langle c_i(\mathbf{r}) \rangle_{\rm id} \tag{37}$$

$$\Phi_\alpha(\mathbf{r}) \;=\; v \langle C_\alpha(\mathbf{r}) \rangle_{\rm id} = v_{\alpha i} \phi_i(\mathbf{r}) \quad . \tag{38}$$

for all $i, \alpha = 1, \ldots, M$. Because these are evaluated for a gas with an external potential $H_{\rm c}$, these volume fraction fields are functionals of the w fields.

Functional Derivatives

Expressions for functional derivatives of H with respect to the auxiliary fields are needed to identify saddle-point field configurations and to design Langevin simulations. Let $D_\alpha(\mathbf{r})$ denote the functional derivative

$$D_\alpha(\mathbf{r}) = \frac{1}{\sigma_\alpha}\frac{\delta H}{\delta \omega_\alpha(\mathbf{r})} = \frac{\delta H}{\delta \Omega_\alpha(\mathbf{r})} \quad , \tag{39}$$

for any $\alpha = 1, \ldots, M$, with $\sigma_M = i$. A straightforward calculation that is presented in supporting information (SI) yields

$$D_\alpha(\mathbf{r}) = \frac{1}{v}\left[-\frac{M}{\lambda_\alpha}\Omega_\alpha(\mathbf{r}) + \Phi_\alpha(\mathbf{r})\right] \tag{40}$$

for all $\alpha = 1, \ldots, M-1$, and

$$D_M(\mathbf{r}) = \frac{1}{v}\left[\Phi_M(\mathbf{r}) - 1\right] \quad , \tag{41}$$

for $\alpha = M$, where $\Phi_M(\mathbf{r}) = v\langle C_M(\mathbf{r})\rangle_{\mathrm{id}}$.

Saddle-points of h are field configurations for which $D_\alpha(\mathbf{r}) = 0$ for all $\mathbf{r}$ and all $\alpha = 1, \ldots, M$. We confirm in the SI that the resulting set of saddle-point equations is equivalent to the conventional formulation of the SCF equations for monomer species in terms of volume fractions $\phi_1, \ldots, \phi_M$.

Structure Factor

Let $S_{ij}(\mathbf{k})$ denote the structure factor matrix

$$S_{ij}(\mathbf{k}) \equiv \frac{1}{V}\langle \delta\hat{c}_i(\mathbf{k})\delta\hat{c}_j(-\mathbf{k})\rangle \quad , \tag{42}$$

where $\mathbf{k}$ is a wavevector and

$$\delta\hat{c}_i(\mathbf{k}) = \int d\mathbf{r}\; e^{-i\mathbf{k}\cdot\mathbf{r}}\delta c_i(\mathbf{r}) \quad . \tag{43}$$

denotes the Fourier transform of the concentration fluctuation $\delta c_i(\mathbf{r}) = c_i(\mathbf{r}) - \langle c_i(\mathbf{r})\rangle$. It is shown in SI that the structure function of an an incompressible system can be expressed for any $M \geq 2$ as a sum

$$S_{ij}(\mathbf{k}) \equiv \sum_{\alpha\beta=1}^{M-1} v_{\alpha i} v_{\beta j} \left\{ \frac{1}{v^2 \lambda_\alpha \lambda_\beta} G_{\alpha\beta}(\mathbf{k}) - \frac{1}{vM\lambda_\alpha}\delta_{\alpha\beta} \right\} \tag{44}$$

in which

$$G_{\alpha\beta}(\mathbf{k}) = \frac{1}{V}\langle \delta\hat{W}_\alpha(\mathbf{k})\delta\hat{W}_\beta(-\mathbf{k})\rangle \quad , \tag{45}$$

and $\delta\hat{W}_\alpha(\mathbf{k})$ is the Fourier transform of $\delta W_\alpha(\mathbf{r}) = W_\alpha(\mathbf{r}) - \langle W_\alpha(\mathbf{r})\rangle$.

Two Monomer (AB) Systems

Consider a system with two types of monomer, $M = 2$, which we refer to as an AB system. Previous PS-FTS numerical studies have only considered this case. For $M = 2$, the subspace orthogonal to $\mathbf{e}$ is one dimensional, and is spanned by a vector

$$\mathbf{v} = \mathbf{v}_1 = [1, -1]^T \quad , \tag{46}$$

giving a projection matrix

$$\mathbf{P} = \frac{1}{2}\mathbf{v}_1\mathbf{v}_1^T = \frac{1}{2}\begin{bmatrix} 1 & -1 \\ -1 & 1 \end{bmatrix} \quad . \tag{47}$$

Suppose we have a generic symmetric unprojected χ matrix with elements denoted by χ_{ij}, with $\chi_{12} = \chi_{21}$. The corresponding projected χ matrix can be expressed as a product

$$\tilde{\boldsymbol{\chi}} = -\chi \mathbf{P} \tag{48}$$

in which we have defined a scalar χ parameter

$$\chi \equiv -\mathbf{v}_1^T \boldsymbol{\chi} \mathbf{v}_1 / 2 = \frac{1}{2}[2\chi_{12} - \chi_{11} - \chi_{22}] \quad . \tag{49}$$

The resulting matrix $\tilde{\boldsymbol{\chi}}$ has a single nonzero eigenvalue $\lambda_1 = -\chi$ associated with eigenvector $\mathbf{v}_1$, and constant values $S_1 = (\chi_{11} - \chi_{22})/4$ and $S_2 = (2\chi_{12} + \chi_{11} + \chi_{22})/4$.

We focus in the remainder of this section on systems that satisfy the convention for interaction parameters used in previous simulation studies, in which $\chi_{11} = \chi_{22} = 0$ and $\chi_{12} = \chi_{21} = \chi$. We refer this here as a standard AB system. For such systems, the symmetric formalism yields $S_1 = 0$ and $S_2 = \chi/2$. If we adopt notation analogous to that of Matsen and Beardsley (MB),[11] in which the subscripts 1 and 2 are replaced by $-$ and $+$, so that $\omega_- = \omega_1$ and $\omega_+ = \omega_2$, we obtain monomer fields

$$\begin{aligned} w_1(\mathbf{r}) &= +\omega_-(\mathbf{r}) + i\omega_+(\mathbf{r}) \\ w_2(\mathbf{r}) &= -\omega_-(\mathbf{r}) + i\omega_+(\mathbf{r}) \quad , \end{aligned} \tag{50}$$

in analogy to Eq. (17) of MB,[11] and a Hamiltonian

$$H = -\ln Z_{\rm id} + \frac{1}{v}\int d\mathbf{r} \, \left\{ \frac{\omega_-^2}{\chi} - i\omega_+ + \frac{\chi}{4} \right\} \quad , \tag{51}$$

in analogy to their Eq. (12). The symmetric formulation given here thus reduces for standard AB systems to the formulation used by previous authors.

Three Monomer (ABC) Systems

We now consider the behavior of the eigenvalues of the projected matrix $\tilde{\boldsymbol{\chi}}$ for a system with three monomer types, $M = 3$, which we refer to as an ABC system. We focus here on how the number of positive or negative eigenvalues of $\tilde{\boldsymbol{\chi}}$ depends on the values of the binary interaction parameters. For simplicity, we assume throughout this section that, by convention, diagonal elements of the full χ matrix vanish, so that $\chi_{11} = \chi_{22} = \chi_{33} = 0$.

General Analysis

The projected χ matrix for a system with $M = 3$ is a singular 3×3 matrix that, by construction, has one vanishing eigenvalue associated with eigenvector $\mathbf{e}$. We focus hereafter on the two remaining nontrivial eigenvalues, whose values depend on the values of the interaction parameters.

In a calculation that is presented in the SI, we show how an orthogonal transformation of $\tilde{\boldsymbol{\chi}}$ to any basis in which one of the basis vectors is colinear with $\mathbf{e}$ transforms this matrix to a form that in which all nonzero elements lie in a 2×2 block. The eigenvalues of this remaining 2×2 block are then the desired nontrivial eigenvalues of $\tilde{\boldsymbol{\chi}}$. These two eigenvalues are given by the roots of a quadratic equation, which are denoted here by λ_- and λ_+, with $\lambda_- < \lambda_+$. Because the labelling of monomers is arbitrary, and the symmetric formulation considered here preserves the symmetry under permutations of monomer types labels, the eigenvalues are conveniently expressed in terms of three quantities

$$\begin{aligned} L &\equiv \chi_{12} + \chi_{13} + \chi_{23} \\ K &\equiv \chi_{12}^2 + \chi_{13}^2 + \chi_{23}^2 \\ J &\equiv \chi_{12}\chi_{13} + \chi_{12}\chi_{23} + \chi_{13}\chi_{23} \end{aligned} \tag{52}$$

that are invariant under such permutations of labels, with $L^2 = K + 2J$. A calculation

presented in SI yields two nontrivial eigenvalues

$$\lambda_{\pm} = \frac{1}{3}\left(-L \pm 2\sqrt{K - J} \right) \quad . \tag{53}$$

It is straighforward to show that the product of these two eigenvalues is given by

$$\lambda_{-}\lambda_{+} = (2J - K)/3 \quad . \tag{54}$$

This product is positive, indicating that these two eigenvalues have the same sign, if and only if $2J > K$. In the usual case in which the sum of the three χ parameters is positive (i.e., when $L > 0$), the smaller eigenvalue λ_{-} is always negative, and so the larger eigenvalue λ_{+} is also negative if $2J > K$.

Jiang, Xu and Zhang (JXZ)[16] have previously considered how the analytic character of the SCFT saddle point for incompressible ABC systems depends on the values of the Flory-Huggins χ parameters. Their analysis was performed using an MSE formalism similiar to that of Düchs, Delaney and Fredrickson.[5] JXZ obtained an expression for the surface along which the index of this saddle point changes that is equivalent to the expression obtained here for the surface along which $\lambda_{+} = 0$, as given by Eq. (53) or (54).

To visualize regions in the space of χ parameter values, it is convenient to adopt a convention for monomer labels for which χ_{13} is the interaction parameter of greatest absolute magnitude ($|\chi_{13}| > |\chi_{12}|, |\chi_{23}|$) and consider the dependence on the two ratios $\hat{\chi}_{12} \equiv \chi_{12}/\chi_{13}$ and $\hat{\chi}_{23} \equiv \chi_{23}/\chi_{13}$. With this convention, both of these ratios must lie in the range $[-1, 1]$. By rewriting Eq. (54) in terms of these ratios, we find that $\lambda_{-}\lambda_{+} > 0$ if and only if

$$2\left(\hat{\chi}_{12} + \hat{\chi}_{23}\right) > 1 + \left(\hat{\chi}_{12} - \hat{\chi}_{23}\right)^2 \tag{55}$$

The regions separated by this separatrix in the $\hat{\chi}_{12}$-$\hat{\chi}_{23}$ plane are shown in Fig. 1. The separatrix terminates at end end-points $(0, 1)$ and $(1, 0)$ and intersects the symmetry line

$\hat{\chi}_{12} = \hat{\chi}_{23}$ at the point $(1/4, 1/4)$.

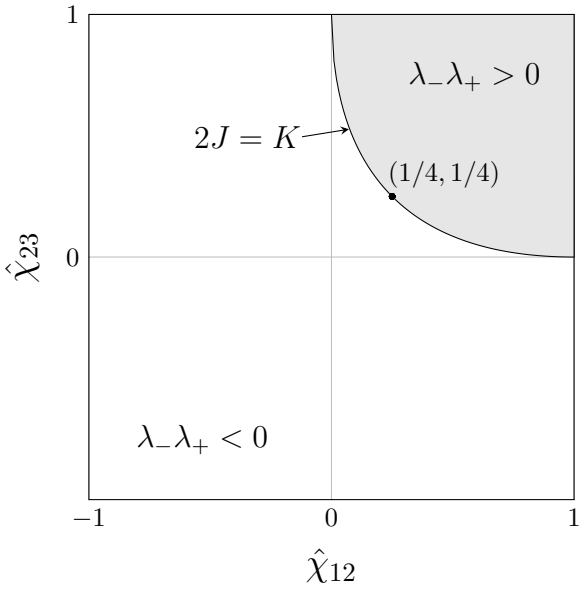

Figure 1: Regions for an three monomer system in which the projected χ matrix $\tilde{\boldsymbol{\chi}}$ has two nontrivial eigenvalues λ_- and λ_+ of the same sign (gray region in which $\lambda_+\lambda_- > 0$) or of opposite sign (white region in which $\lambda_+\lambda_- < 0$) in a plane with coordinates $\hat{\chi}_{12} = \chi_{12}/\chi_{13} \in [-1, 1]$ and $\hat{\chi}_{23} = \chi_{12}/\chi_{13} \in [-1, 1]$. Here, χ_{13} is the interaction parameter of greatest absolute magnitude, $|\chi_{13}| > |\chi_{12}|, |\chi_{23}|$. These two regions are separated by a curve along which $2J = K$, one which one of the eigenvalues passes through zero. The gray region in which $\lambda_+\lambda_- > 0$ is contained within the quadrant with $\hat{\chi}_{12} > 0$ and $\hat{\chi}_{23} > 0$ in which all three interaction parameters are of the same sign. This region yields two negative eigenvalues in the common case of three positive χ parameters.

The upper right quadrant of Fig. (1) is the only region in which all three χ parameters have the same sign (i.e., all positive or all negative). The remaining three quadrants represent regions in which there exist χ parameters of both signs. Note that systems with χ parameters of both signs always yield $\lambda_-\lambda_+ < 0$, indicating the existence of nontrivial eigenvalues of opposite signs. The two nontrivial eigenvalues are of the same sign only within the region in the upper right quadrant that is shown in gray, within which all three χ parameters are of the same sign and not too disparate in magnitude. When all three χ parameters are positive, interaction parameter values in this region yield two negative eigenvalues. When all three χ parameters are negative, values in this region instead yields two positive eigenvalues.

Hildebrand Approximation

Values for binary χ parameters in polymeric systems with simple non-polar chemical repeat units can often be approximated by the Hildebrand solubility parameter approximation.[17] This approximation predicts an interaction parameter for monomer types i and j given by

$$\chi_{ij} = \frac{v}{kT}(\delta_i - \delta_j)^2 \quad . \tag{56}$$

where δ_i and δ_j are solubility parameters that are properties of corresponding homopolymer melts.

The Hildebrand approximation introduces a constraint on the possible values of the binary χ parameters, and thus on the eigenvalues of the matrix $\tilde{\boldsymbol{\chi}}$. To analyze the implications of this constraint in an ABC system, it is convenient to label the monomer types such that $\delta_1 < \delta_2 < \delta_3$, define $\Delta = \delta_3 - \delta_1$, and define parameters α and β such that

$$\delta_2 - \delta_1 = \alpha\Delta \qquad \delta_3 - \delta_2 = \beta\Delta \quad , \tag{57}$$

such that $\alpha, \beta \in [0, 1]$ and $\alpha + \beta = 1$. This gives χ parameters

$$\chi_{13} = v\Delta^2/kT \qquad \chi_{12} = \alpha^2\chi_{13} \qquad \chi_{23} = \beta^2\chi_{13} \quad . \tag{58}$$

Using these definitions, we show in SI that the permutational invariants K and J satisfy

$$K = 2J = 2\chi_{13}^2(1 + \alpha^2\beta^2 - 2\alpha\beta) \quad . \tag{59}$$

Because this gives $2J = K$, it yields

$$\lambda_-\lambda_+ = (2J - K)/3 = 0 \tag{60}$$

for any value of α.

This analysis thus shows that the Hildebrand approximation always predicts a vanishing value for one or both of the two nontrivial eigenvalues λ_- and λ_+. For any system with unequal solubility parameters, and thus $\Delta > 0$, the Hildebrand approximation yields $L > 0$, and thus always yields one negative eigenvalue, $\lambda_- < 0$ and one vanishing eigenvalue, $\lambda_+ = 0$. Only the special case $\Delta = 0$, for which all interaction parameters vanish, yields $\lambda_- = \lambda_+ = 0$.

The Hildebrand approximation for ABC systems thus yields an unusual situation that deserves closer consideration. To generalize slightly, consider a system with M monomers in which one nontrivial eigenvalue λ_α with $\alpha < M$ happens to equal zero. This occurs for $M = 2$ when $\chi = 0$ and for $M = 3$ when the interaction parameters satisfy the equality $K = 2J$. When $\lambda_\alpha = 0$ for a particular eigenvalue, fluctuations of the associated auxiliary field ω_α are completely suppressed by the appearance of a divergent factor of $1/\lambda_\alpha$ that appears as a prefactor of the term quadratic in ω_ω in Eq. (27) for $H_{\rm f}$. This yields a statistical ensemble in which the only field configurations with nonzero weight are those for which $\omega_\alpha(\mathbf{r}) = 0$ for all $\mathbf{r}$. The functional integral for Z in a fully fluctuating theory can thus be formulated in this special case by simply setting $\omega_\alpha(\mathbf{r}) = 0$ in the Hamiltonian, and expressing the functional integral as an integral only over the remaining $M - 1$ auxiliary fields, which always include the pressure-like field ω_M.

For an ABC system that obeys the Hildebrand approximation with $\Delta > 0$, for which $\lambda_+ = 0$, we thus obtain a functional integral over a real field $\Omega_1 = \omega_1$ associated with the negative eigenvalue λ_- and over an imaginary pressure-like field component $\Omega_3 = i\omega_3$ that imposes incompressibility. The theory thus reduces in this special case to a form very similar to that found for an AB system with $\chi > 0$.

Partial Saddle-Point Approximation

We now define and discuss a generalization of the partial saddle-point approximation (PSA) so as to apply to systems with $M > 2$. The PSA has previously been applied only to

incompressible AB systems, with $M = 2$.

Definition of PSA

AB Systems: We first review the PSA for AB systems with $\chi > 0$. In the PSA for such a system, one ignores fluctuations in the imaginary field ω_+ (or ω_2) and evaluates the Hamiltonian using a partial saddle-point configuration of $\omega_+(\mathbf{r})$, while allowing ω_- (or ω_1) to fluctuate. A partial saddle-point field configuration is defined by the requirement that functional derivative of H with respect to ω_+ at fixed ω_- must vanish, i.e., that

$$0 = \frac{\delta H[\omega_-, \omega_+]}{\delta \omega_+(\mathbf{r})} \tag{61}$$

for all $\mathbf{r}$. Let ω_+^* denote the partial-saddle point configuration of the field ω_+ that satisfies this condition, which is itself a functional of ω_-. The PSA for the partition function Z for such a system is given by an functional integral over the exchange field ω_-, as

$$Z = N^{-1} \int \mathcal{D}\omega_1 e^{-H[\omega_-, \omega_+^*]} \tag{62}$$

in which ω_+^* is the partial saddle-point configuration of $\omega_+(\mathbf{r})$ at the specified configuration of $\omega_-(\mathbf{r})$. For incompressible AB systems with $\chi > 0$, it appears that there always exists a solution to the partial saddle-point equation for which $i\omega_+(\mathbf{r})$ is a real field. Use of this partial saddle-point value for ω_+ then yields real values for the monomer chemical potential fields $w_1(\mathbf{r})$ and $w_2(\mathbf{r})$ and for the Hamiltonian $H[\omega_-, \omega_+^*]$. The existence of a real Hamiltonian allows the use of conventional Monte Carlo and Brownian dynamics sampling methods, and avoids the "sign problem" found in the fully fluctuating theory.

Generalized PSA: It is straightforward to formulate a generalized PSA for systems with $M \geq 2$ by analogy to the case $M = 2$. To do so, we divide the list of M fields $\omega_1, \ldots, \omega_M$ into one list of fields for which the corresponding eigenvalues of $\tilde{\boldsymbol{\chi}}$ are negative, which we denote collectively by ω_-, and a second list of fields for the corresponding eigenvalues of $\tilde{\boldsymbol{\chi}}$

are positive or zero, which we will denote by ω_+. The list ω_+ always contains the constraint field ω_M, and may also include one more fields $\omega_1, \ldots, \omega_{M-1}$ that are associated with positive eigenvalues of $\tilde{\boldsymbol{\chi}}$.

Suppose that the symmetric matrix $\tilde{\boldsymbol{\chi}}$ has L negative eigenvalues for which $\sigma_\alpha = 1$ and and $M - L$ non-negative (positive or zero) eigenvalues for which $\sigma_\alpha = i$, with $L < M$. By convention, we order the eigenvalues so that $\alpha_1, \ldots, \alpha_L$ are negative, so that $\omega_- = (\omega_1, \ldots, \omega_L)$ and $\omega_+ = (\omega_{L+1}, \ldots, \omega_M)$.

The generalized PSA for an incompressible system with $M \geq 2$ is given by a straightforward generalization of Eq. (62), in which the treatments of the fields ω_- and ω_+ is generalized so as to apply to the corresponding lists of fields with the same names. In general, Z is defined as a functional integral over over the L fields in list ω_-, which are thus allowed to fluctuate, while the field theoretic Hamiltonian is evaluated using partial saddle-point values for all of the fields in list ω_+. A partial saddle-point field configuration is defined as one in which the functional derivative of $H[\omega_1, \ldots, \omega_M]$ with respect to field ω_α vanishes for all fields in list ω_+ corresponding to $\alpha = L+1, \ldots, M$. This formulation assumes that, for each configuration of the fields in list ω_-, there exists a unique partial saddle-point configuration of the fields in list ω_+ for which $i\omega_\alpha$ is real for all $\alpha = L+1, \ldots, M$, giving a partial saddle-point configuration with real monomer fields.

Discussion of PSA

The additional approximation involved in applying this generalized PSA to systems with $M \geq 2$, compared to the case $M = 2$, is the application of a partial saddle-point (or self-consistant field) approximation to field components associated with positive eigenvalues of $\tilde{\boldsymbol{\chi}}$, if any. Each negative eigenvalue λ_α of $\tilde{\boldsymbol{\chi}}$, with $\alpha \leq L$, corresponds to a negative contribution to the potential energy U of the particle based model that arises from fluctuations of a corresponding monomer concentration component $C_\alpha(\mathbf{r})$. Terms associated with negative eigenvalues thus acts to enhance fluctuations of associated concentration field components.

Auxiliary field components associated with negative eigenvalues of $\tilde{\boldsymbol{\chi}}$ are thus "dangerous" modes that can lead to strong correlations and microphase separation, indicating that we should prioritize the explicit treatment of these field components in field theoretic simulations. Each positive eigenvalue of $\tilde{\boldsymbol{\chi}}$ is, however, associated with a negative contributions to U that instead acts to *suppress* the magnitude of fluctuations of an associated concentration field component. The generalized PSA described above thus applies a self-consistent field approximation to all auxiliary chemical potential field components that arise from potential energy contributions that act to suppress (rather than enhance) fluctuations of an associated concentration component. If applied to a standard AB system with $M = 2$, this generalized PSA would require explicit sampling of fluctuations of ω_- and a PSA for ω_+ for systems $\chi > 0$, but would reduce to SCFT (i.e., use of PSA for both field components) for AB systems with $\chi < 0$.

To clarify some consequences of the PSA, consider its application to a particular field component ω_α associated with an eigenvalue $\lambda_\alpha > 0$, and then consider the limits $\lambda_\alpha \to 0^+$ and $\lambda_\alpha \to +\infty$. In the limit $\lambda_\alpha \to 0^+$, fluctuations of $\omega_\alpha(\mathbf{r})$ are entirely suppressed by the prefactor of $1/\lambda_\alpha$ in the term in H_f that involves fluctuations of component ω_α. In this limit, application of the PSA to component ω_α thus actually becomes exact. In the opposite limit $\lambda_\alpha \to +\infty$, fluctuations of $\omega_\alpha(\mathbf{r})$ are generally not small, but their physical effect is to completely suppress fluctuations of the associated concentration field component $C_\alpha(\mathbf{r})$, effectively imposing a constraint on this concentration component. In this limit $\lambda_\alpha \to +\infty$, application of the PSA to a component with $L < \alpha < M$ thus becomes completely analogous to the use of a field component ω_M to impose a rigorous constrain on the total monomer concentration C_M. Application of the PSA might naturally be expected to be least accurate in this latter limit of a large positive eigenvalue as that obtained when applied to the field component ω_M (corresponding to the worst-case scenario of an infinite positive eigenvalue) and to be more accurate for small positive eigenvalues that for large positive eigenvalues. Experience with AB systems suggests, however, that use of the PSA to approximate the

incompressibility constraint appears to yield rather accurate results when applied to polymeric systems with a large invariant degree of polymerization, $\overline{N} \to \infty$, and when interpreted properly.

A thorough discussion of the reasons for the apparent effectiveness of the PSA to treat the incompressibility constraint in AB systems is beyond the scope of this paper. We comment here only that the this effectiveness is presumably only valid for systems with large values of $\overline{N}$, and is probably related in part to the fact that the associated concentration fluctuations at relevant wavelengths of order the polymer coil size become small in the limit $\overline{N} \to \infty$ even for the non-interacting reference system used in the PSA, thereby allowing treatment of a constraint at a self-consistent-field level to yield accurate results for many quantities in the limit of sufficiently large values of $\overline{N}$. The above discussion of the physics of the PSA in the limits of small and large positive eigenvalues of $\tilde{\boldsymbol{\chi}}$, together with experience over the last decade with the behavior of the PSA in AB systems, suggests that the PSA could well yield useful predictions for systems with $\overline{N} \gg 1$ when applied to any field component ω_α for which $\lambda_\alpha > 0$, as proposed above. This is, of course, not a proof, but merely an argument for guarded optimism and further study.

A particularly strong case for the potential usefulness of a generalized PSA can be made for ABC systems ($M = 3$) for which the binary interaction parameters nearly obey the Hildebrand approximation. For concreteness, imagine an ABC system for which all of the interaction parameters are positive in which we order the eigenvalues of $\tilde{\boldsymbol{\chi}}$ assigning an index $\alpha = 1$ to the eigenvalue λ_-, which must be negative, assigning $\alpha = 2$ to the eigenvalue λ_+, which is small but could be either positive or negative, and $\alpha = 3$ to the zero eigenvalue associated with eigenvector $\mathbf{e} = \mathbf{v}_3$. In an ABC system that exactly obeys the Hildebrand approximation, $\lambda_1 < 0$ but $\lambda_2 = 0$, and so fluctuations of field component $\omega_2(\mathbf{r})$ are completely suppressed. Application of the PSA to ω_2 is thus exact in this case. In cases in which λ_2 is small but negative, the PSA is applied only to the pressure-like field ω_3, as for an AB system, and so we expect the PSA to yield an accuracy similar to that typically obtained

in PS-FTS studies of AB systems. In cases in which λ_2 is small but positive, the PSA is applied to an additional field ω_2 for which fluctuations in fully fluctuating theory are also small, so that the use of the PSA for this component should be accurate, and so we again expect to obtain an accuracy similar to that typical of an AB system. Application of the generalized PSA to any ABC system for which the χ parameters nearly obey the Hildebrand approximation (with deviations of either sign) should thus be expected to yield an accuracy comparable to that obtained for AB systems.

Weakly Compressible Model

We now show how a symmetric formulation of the theory for an incompressible model similar to that presented here be obtained by starting from a compressible model and considering the limit of vanishing compressibility (or infinite compression modulus). Consider a compressible model with a a potential energy of the form $U = U_{\rm id} + U_{\rm int} + U_{\rm ext}$, in which

$$U_{\rm int} = \frac{v}{2} \int d\mathbf{r} \, \{ \, \chi_{ij} c_i c_j + \zeta (e_i c_i - c_0)^2 \, \} \tag{63}$$

$$U_{\rm ext} = - \int d\mathbf{r} \, y_i c_i \quad , \tag{64}$$

where ζ is a dimensionless compression modulus, $e_i c_i$ is the total monomer concentration that we denoted by C_M in the incompressible theory, and $c_0 = 1/v$ is the energetically preferred value for this total monomer concentration. Here, $y_i(\mathbf{r})$ is an external source field associated with monomer type i. This interaction energy may also be expressed as a sum

$$U_{\rm int} = \int d\mathbf{r} \left\{ \, \frac{v}{2} U_{ij} c_i c_j - \zeta e_i c_i \, \right\} + U_{\rm int}^{(0)} \quad , \tag{65}$$

in which we have defined a matrix $\mathbf{U}$ with elements

$$U_{ij} = \chi_{ij} + \zeta e_i e_j \quad , \tag{66}$$

while $U_{\rm int}^{(0)} = \zeta V c_0/2$.

Compressible Field Theory

When analyzing this model, we expand all fields in a basis of eigenvectors of the matrix $\mathbf{U}$ with elements U_{ij}. For any $\alpha = 1, \ldots, M$, let

$$\mathbf{U}\mathbf{x}_\alpha = \kappa_\alpha \mathbf{x}_\alpha \tag{67}$$

where $\mathbf{x}_\alpha$ and κ_α denote an eigenvector and associated eigenvalue, for which $\mathbf{x}_\alpha^T \mathbf{x}_\beta = M\delta_{\alpha\beta}$. We define a concentration component $C_\alpha(\mathbf{r}) = \mathbf{x}_\alpha^T \mathbf{c}(\mathbf{r})$ for each $\alpha = 1, \ldots, M$, where $\mathbf{c}(\mathbf{r}) = [c_1(\mathbf{r}), \ldots, c_M(\mathbf{r})]^T$ is a vector of monomer concentrations. By expanding $\mathbf{c}(\mathbf{r})$ in this basis, we obtain

$$\begin{aligned} U_{\rm int} &= \sum_{\alpha=1}^{M} \int d\mathbf{r}\ \left\{ \frac{\upsilon \kappa_\alpha}{2M} C_\alpha^2 - \zeta E_\alpha C_\alpha \right\} + U_{\rm int}^{(0)} \\ U_{\rm ext} &= -\sum_{\alpha=1}^{M} \int d\mathbf{r}\ Y_\alpha C_\alpha \quad , \end{aligned} \tag{68}$$

in which

$$E_\alpha \equiv x_{\alpha i} e_i / M \qquad Y_\alpha(\mathbf{r}) \equiv x_{\alpha i} y_i(\mathbf{r})/M \tag{69}$$

Applying a Hubbard-Stratonovich transformation to the quadratic terms in this model, by introducing auxiliary fields $\psi_1, \ldots, \psi_M$, yields an expression for Z as a functional integral with a field-theoretic Hamiltonian

$$\begin{aligned} H[\psi] &= -\ln Z_{\rm id} + H_{\rm f} \\ H_{\rm f} &= \sum_{\alpha=1}^{M} \int d\mathbf{r} \frac{M\psi_\alpha^2}{2\upsilon|\kappa_\alpha|} + U_{\rm int}^{(0)} \end{aligned} \tag{70}$$

in which $Z_{\mathrm{id}}[W]$ is the partition function of an ideal gas that is subjected to an external potential

$$H_{\mathrm{c}} = \sum_{\alpha=1}^{M} W_\alpha(\mathbf{r}) C_\alpha(\mathbf{r}) \quad , \tag{71}$$

where

$$W_\alpha(\mathbf{r}) = \Psi_\alpha(\mathbf{r}) - \zeta E_\alpha - Y_\alpha \tag{72}$$

$$\Psi_\alpha(\mathbf{r}) = \sigma_\alpha \psi_\alpha(\mathbf{r}) \quad , \tag{73}$$

with $\sigma_\alpha = 1$ for $\kappa_\alpha < 0$ and $\sigma_\alpha = i$ for $\kappa_\alpha > 0$.

Incompressible Limit ($\zeta \to \infty$)

To describe an incompressible fluid, we consider a limiting process in which all elements of $\boldsymbol{\chi}$ are held constant while $\zeta \to +\infty$. As ζ increases, we find that one eigenvalue of $\mathbf{U}$ diverges while the others approach finite limits. By convention, we assign indices $1, \ldots, M-1$ to the eigenvalues that remain finite in this limit, and an index M to the diverging eigenvalue. We show in SI that, in the limit $\zeta \to \infty$:

- Eigenvector $\mathbf{x}_M$ approaches $\mathbf{e}$, while the associated eigenvalue κ_M diverges, such that $\kappa_M/(M\zeta) \to 1$.
- For $\alpha = 1, \ldots, M-1$, each eigenvector $\mathbf{x}_\alpha$ and eigenvalue κ_α of $\mathbf{U}$ approach a corresponding eigenvector $\mathbf{v}_\alpha$ and eigenvalue λ_α of the projected chi matrix $\tilde{\boldsymbol{\chi}}$.

The fact that $\mathbf{x}_M \to \mathbf{e}$ in this limit implies that $E_M \to 1$. The orthogonality of eigenvalues of $\mathbf{U}$ thus also implies that $E_\alpha \to 0$ for $\alpha < M$. It is shown in SI that values of E_α for $\alpha < M$ decrease as $1/\zeta$ with increasing ζ, such that

$$\lim_{\zeta \to \infty} \zeta E_\alpha = -S_\alpha \tag{74}$$

for all $\alpha < M$. Observe that Eq. (74) implies that, for all $\alpha < M$, the quantity $-\zeta E_\alpha$ that appears on the RHS of Eq. (72) for $W_\alpha(\mathbf{r})$ in compressible theory will approach the quantity S_α that appears in the analogous position within Eq. (30) for $W_\alpha(\mathbf{r})$ in the incompressible theory.

It is also possible to establish correspondences between values of fluctuating variables in corresponding field configurations of the compressible and incompressible theories. For this purpose, we define "corresponding states" of the compressible and incompressible theories to be states with equal values for all monomer chemical potential fields $w_1(\mathbf{r}), \ldots, w_M(\mathbf{r})$, as well as equal values for the χ parameters and all monomer source fields $y_1(\mathbf{r}), \ldots, y_M(\mathbf{r})$. To characterize the incompressible limit of the weakly-compressible theory, we consider a hypothetical limiting process in which the χ matrix, the y fields and w fields are all held constant while ζ approaches $+\infty$. In what follows, a fluctuating variable A that is defined in the compressible theory is said to be "asymptotically equivalent" to a corresponding variable B that is defined in the incompressible theory if A approaches a limit as $\zeta \to \infty$ that is equal to the value of B in a corresponding state of the incompressible theory.

An analysis of the behavior of a variety of variables in the limit $\zeta \to \infty$ is presented in SI. That analysis establishes the following asymptotic relationships:

- For all $\alpha < M$, the value of $\Psi_\alpha(\mathbf{r})$ in the compressible theory is asymptotically equivalent to the value of $\Omega_\alpha(\mathbf{r})$ in the incompressible theory.

- The value of the Hamiltonian $H[\psi]$ of the compressible theory is asymptotically equivalent to the value of the Hamiltonian $H[\omega]$ of the incompressible theory.

- The quantity $\Psi_M(\mathbf{r}) - \zeta$ in the compressible theory is asymptotically equivalent to the value of $\Omega_M(\mathbf{r})$ in the incompressible theory.

As one result of the asymptotic equivalence of Hamiltonian values of the two theories, and equivalence of corresponding fields to within a constant in the pressure-like field, the functional derivative $\delta H/\delta\Psi_\alpha$ of the compressible theory can also be shown to be asymptoti-

cally equivalent to the corresponding derivative $\delta H/\delta\Omega_\alpha$ of the compressible theory, for all $\alpha = 1, \ldots, M$.

The asymptotic equivalence of values of H in corresponding states of fully fluctuating compressible and incompressible theories implies that corresponding states will be assigned asymptotically equivalent equal statistical weights in a fully fluctuating complex Langevin field theoretic simulation (CL-FTS) of either theory. The asymptotic equivalence of functional derivatives of H also implies that the two theories exhibit asymptotically equivalent partial-saddle point field configurations, and thus that asymptotically equivalent weights will be assigned to corresponding partial saddle-point configurations of PS-FTS simulations of compressible and incompressible models. The compressible theory presented here is thus asymptotically equivalent to the incompressible theory of section 2 in the sense that the two theories yield asymptotically equivalent statistical weights for corresponding states in either CL-FTS or in PS-FTS methods.

The only notable formal difference between the incompressible limit of the compressible model and the incompressible model of section 2 is the existence of a spatially homogeneous difference between the value of the pressure-like field $\Psi_M(\mathbf{r}) = i\psi_M(\mathbf{r})$ in the compressible theory and the value of $\Omega_M(\mathbf{r}) = i\omega_M(\mathbf{r})$ in a corresponding state of the incompressible theory. The existence of such a homogeneous difference becomes clear upon comparing of Eq. (72), which yields $\Psi_M(\mathbf{r}) = W_M(\mathbf{r}) + Y_M(\mathbf{r}) + \zeta E_M$ in the compressible theory, to Eq. (31), which yields $\Omega_M(\mathbf{r}) = W_M(\mathbf{r}) + Y_M(\mathbf{r})$ in the incompressible theory, while noting that $E_M \to 1$ as $\zeta \to \infty$. This homogeneous shift could be removed without changing the physical content of either theory by (among other possible methods) deforming the integration contour for $\Psi_M(\mathbf{r})$ in the compressible theory so as to make $\Psi_M(\mathbf{r}) - \zeta$ a pure imaginary field.

Conclusions

We have presented a "symmetric" formulation of field theory for incompressible polymer systems with any number of monomer types, in which incompressibility is applied in a manner that manifestly preserves the symmetry among different monomer types. Both the fully fluctuating theory and a generalized partial saddle-point approximation have been discussed. The symmetric formulation is based on the introduction of a projected χ matrix that describes how the binary interaction energy changes in response to changes in monomer concentrations that respect the incompressibility constraint. The symmetric formulation has been shown to emerge naturally from an analysis of the incompressible limit of a compressible model, and to also reduce to the existing formulation for standard AB systems when applied to such systems. This formulation is proposed as a convenient theoretical basis for the development of software for PS-FTS of incompressible models for systems with an arbitrary number of monomer types, and is now being incorporated into two different software packages maintained by the authors.

We have discussed a straightforward generalization of the PSA to incompressible systems with $M > 2$, in which the PSA is applied to all field components associated with positive or vanishing eigenvalues of the projected χ matrix. Physical arguments are given for why we expect the resulting generalization to often yield accuracy similar to that obtained in PS-FTS studies of AB systems. We do not report any numerical results obtained with this method, deferring that to future work.

An analysis of ABC systems with $M = 3$ has identified the regions in the space of values of the binary χ parameters in which the projected χ matrix has two, one, or zero negative eigenvalues, corresponding to cases that require introduction of one, two or three imaginary-valued fields in a fully fluctuating theory. Incompressible systems with positive values for all χ parameters are found to always require the introduction of either one or two imaginary-valued fields in the fully fluctuating theory, one of which is always required to maintain incompressibility. Systems that obey the Hildebrand solubility-parameter approximation for

the χ parameters are shown to correspond to a special case in which one nontrivial eigenvalue happens to vanish, and in which the fully fluctuating theory requires use of only a single imaginary-valued pressure-like field and a single real-valued exchange field, much like an AB system. Systems with χ parameters that nearly obey the Hildbebrand approximation thus appear to be promising candidates for application of a generalized partial saddle-point approximation, which is expected to lead in these cases to errors very similar to those found in PS-FTS studies of AB systems.

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Supporting Information Available

Supporting information provides mathematical details of some derivations that are only summarized here.

References

(1) Ganesan, V.; Fredrickson, G. Field-theoretic polymer simulations. *Europhys. Lett.* **2001**, *55*, 814–820, DOI: 10.1209/epl/i2001-00353-8.

(2) Fredrickson, G. H.; Ganesan, V.; Drolet, F. Field-Theoretic Computer Simulation Methods for Polymers and Complex Fluids. *Macromolecules* **2002**, *35*, 16–39, DOI: 10.1021/ma011515t.

(3) Fredrickson, G. H. *The Equilibrium Theory of Inhomogeneous Polymers*; Oxford University Press, 2006.

(4) Lennon, E. M.; Katsov, K.; Fredrickson, G. H. Free Energy Evaluation in Field-Theoretic Polymer Simulations. *Physical Review Letters* **2008**, *101*, 138302, DOI: 10.1103/PhysRevLett.101.138302.

(5) Düchs, D.; Delaney, K. T.; Fredrickson, G. H. A multi-species exchange model for fully fluctuating polymer field theory simulations. *J. Chem. Phys.* **2014**, *141*, 174103, DOI: 10.1063/1.4900574.

(6) Delaney, K. T.; Fredrickson, G. H. Recent Developments in Fully Fluctuating Field-Theoretic Simulations of Polymer Melts and Solutions. *J. Phys. Chem. B* **2016**, *129*, 7615–7634, DOI: 10.1021/acs.jpcb.6b05704.

(7) Fredrickson, G. H.; Delaney, K. T. Direct free energy evaluation of classical and quantum many-body systems via field theoretic simulations. *Proceedings of the National Academy of Sciences* **2022**, *119*, e2201804119, DOI: 10.1073/pnas.2201804119.

(8) Stasiak, P.; Matsen, M. Monte Carlo Field-Theoretic Simulations for Melts of Symmetric Diblock Copolymers. *Macromolecules* **2013**, *46*, 8037 – 8045, DOI: 10.1021/ma401687j.

(9) Beardsley, T.; Spencer, R.; Matsen, M. Computationally Efficient Field-Theoretic Simulations for Block Copolymer Melts. *Macromolecules* **2019**, *52*, 8840 – 8848, DOI: 10.1021/acs.macromol.9b01904.

(10) Vorselaars, B.; Spencer, R.; Matsen, M. Instability of the Microemulsion Channel in Block Copolymer-Homopolymer Blends. *Phys. Rev. Lett.* **2020**, *125*, 117801, DOI: 10.1103/PhysRevLett.125.117801.

(11) Matsen, M.; Beardsley, T. Field-theoretic simulations of copolymers using the partial saddle-point approximation. *Polymers* **2021**, *13*, 2437, DOI: 10.3390/polym13152437.

(12) Matsen, M.; Beardsley, T.; Willis, J. D. Fluctuation Corrected Phase Diagrams for Diblock Copolymer Melts. *Phys. Rev. Lett.* **2023**, *130*, 248101, DOI: 10.1103/PhysRevLett.130.248101.

(13) Arora, A.; Qin, J.; Morse, D. C.; Delaney, K.; Fredrickson, G. H.; Bates, F. S.; Dorfman, K. D. Broadly accessible self-consistent field theory for block copolymer materials discovery. *Macromolecules* **2016**, *49*, 4675–4690, DOI: 10.1021/acs.macromol.6b00107.

(14) Cheong, G. K.; Chawla, A.; Morse, D. C.; Dorfman, K. D. Open-source code for self-consistent field theory calculations of block copolymer phase behavior on graphics processing units. *European Physical Journal E* **2020**, *43*, 15, DOI: 10.1140/epje/i2020-11938-y.

(15) Yong, D.; Kim, J. Accelerating Langevin field-theoretic simulation of polymers with deep learning. *Macromolecules* **2020**, *55*, 6505–6515, DOI: 10.1021/acs.macromol.2c00705.

(16) Jiang, K.; Xu, W.; Zhang, P. Analytic Structure of the SCFT Energy Functional of Multicomponent Block Copolymers. *Comm. Comput. Phys.* **2015**, *17*, 1360–1487, DOI: 10.4208/cicp.281113.271114a.

(17) Hildebrand, J. H.; Scott, R. L. *The Solubility of Nonelectrolytes*; Dover, 1964.

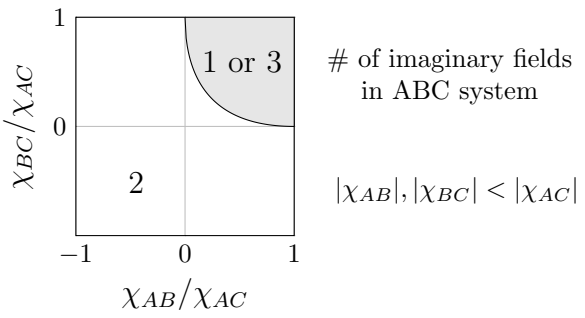

Table-of-Contents Graphical Entry

Supporting Information for "Polymer Field Theory for Multimonomer Incompressible Models: Symmetric Formulation and ABC Systems"

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This document contains a variety of mathematical details of the analyses presented in the associated article.

Incompressible Field Theory

To make this document more self-contained, we begin by restating the main working equations for the incompressible model presented in the second section of the associated article.

Working Equations (Overview)

The projected χ matrix of a system with M monomer types is the symmetric $M \times M$ matrix

$$\tilde{\boldsymbol{\chi}} = \mathbf{P}\boldsymbol{\chi}\mathbf{P} \quad , \tag{1}$$

where

$$\mathbf{P} = \mathbf{I} - \mathbf{Q} \qquad \mathbf{Q} = \mathbf{e}\mathbf{e}^T/M \tag{2}$$

and $\mathbf{e} = [1 \cdots 1]^T$. This is a singular matrix for which $\tilde{\boldsymbol{\chi}}\mathbf{e} = 0$, so $\mathbf{e}$ is an eigenvector with vanishing eigenvalue. For each $\alpha = 1, \ldots, M$, let $\mathbf{v}_\alpha$ and λ_α denote an eigenvector and associated eigenvalue of $\tilde{\boldsymbol{\chi}}$, such that

$$\tilde{\boldsymbol{\chi}}\mathbf{v}_\alpha = \lambda_\alpha \mathbf{v}_\alpha \quad . \tag{3}$$

Let $\mathbf{v}_M = \mathbf{e}$ and $\lambda_M = 0$ by convention. These eigenvectors are normalized such that $\mathbf{v}_\alpha^T \mathbf{v}_\beta = M\delta_{\alpha\beta}$. For $\alpha = 1, \ldots, M-1$, we define

$$\lambda_\alpha = -\sigma_\alpha^2 |\lambda_\alpha| \tag{4}$$

with $\sigma_\alpha = 1$ for $\lambda_\alpha < 0$ and $\sigma_\alpha = i$ for $\lambda_\alpha > 0$. Let $\sigma_M = i$ by convention.

The concentration of monomers of type i is denoted by $c_i(\mathbf{r})$. Components of concentration in an eigenvector basis are denoted by $C_1(\mathbf{r}), \ldots, C_M(\mathbf{r})$, and are defined by relationships

$$C_\alpha(\mathbf{r}) = \sum_{i=1}^{M} v_{\alpha i} c_i(\mathbf{r}) \qquad c_i(\mathbf{r}) = \frac{1}{M}\sum_{\alpha=1}^{M} C_\alpha(\mathbf{r}) v_{\alpha i} \quad , \tag{5}$$

where $v_{\alpha i}$ is the component of eigenvector $\mathbf{v}_\alpha$ associated with monomer type i. We also define a vector $\mathbf{S}$ with components

$$S_\alpha = \frac{1}{M^2}\mathbf{v}_\alpha^T \boldsymbol{\chi}\mathbf{e} \tag{6}$$

for all $\alpha = 1, \ldots, M$. Note that $S_M = \mathbf{e}^T \boldsymbol{\chi} \mathbf{e}/M^2$.

The canonical partition function Z of an incompressible field theory is given by a functional integral

$$Z = N^{-1} \int \mathcal{D}\omega \; e^{-H} \tag{7}$$

$$H = H_{\rm f} - \ln Z_{\rm id} \tag{8}$$

in which

$$H_{\rm f} = \int d^3r \left\{ - \sum_{\alpha=1}^{M-1} \frac{M\Omega_\alpha^2}{2v\lambda_\alpha} - \Omega_M c_0 \right\} + \frac{VS_M}{2v} \tag{9}$$

$$\Omega_\alpha(\mathbf{r}) = \sigma_\alpha \omega_\alpha(\mathbf{r}) \quad , \tag{10}$$

and $Z_{\rm id}[W]$ is the partition function of a hypothetical gas of non-interacting molecules subjected to an external potential $H_{\rm c}$, such that

$$Z_{\rm id}[W] = \int \mathcal{D}\mathbf{r} \; e^{-U_{\rm id} - H_{\rm c}} \tag{11}$$

$$H_{\rm c} = \sum_{\alpha=1}^{M} \int d^3r \; W_\alpha(\mathbf{r}) C_\alpha(\mathbf{r}) \quad , \tag{12}$$

where

$$W_\alpha(\mathbf{r}) = \Omega_\alpha(\mathbf{r}) + S_\alpha - Y_\alpha(\mathbf{r}) \qquad \alpha = 1, \ldots, M-1 \tag{13}$$

$$W_M(\mathbf{r}) = \Omega_M(\mathbf{r}) - Y_M(\mathbf{r}) \quad , \tag{14}$$

while $Y_\alpha(\mathbf{r})$ is an external source field conjugate to $C_\alpha(\mathbf{r})$.

Let $\langle \cdots \rangle_{\rm id}$ denote an average over particle positions for an ideal gas subjected to an external potential $H_{\rm c}$, and let $\phi_i(\mathbf{r})$ and $\Phi_\alpha(\mathbf{r})$ denote average volume fractions fields for

such an ideal gas, defined as

$$\begin{aligned} \phi_i(\mathbf{r}) &= v\langle c_i(\mathbf{r})\rangle_{\rm id} \\ \Phi_\alpha(\mathbf{r}) &= v\langle C_\alpha(\mathbf{r})\rangle_{\rm id} = v_{\alpha i}\phi_i(\mathbf{r}) \end{aligned} \tag{15}$$

for $i = 1, \ldots, M$ and $\alpha = 1, \ldots, M$.

Functional Derivatives of H

Consider the computation of functional derivatives

$$D_\alpha(\mathbf{r}) = \frac{\delta H}{\delta \Omega_\alpha(\mathbf{r})} = \frac{1}{\sigma_\alpha}\frac{\delta H}{\delta \omega_\alpha(\mathbf{r})} \quad , \tag{16}$$

where $H = H_{\rm f} - \ln Z_{\rm id}$. The functional derivative of $-\ln Z_{\rm id}$ with respect to $\Omega_\alpha(\mathbf{r})$ is given for any $\alpha = 1, \ldots, M$ by

$$\begin{aligned} -\frac{\delta \ln Z_{\rm id}}{\delta \Omega_\alpha(\mathbf{r})} &= = \frac{-1}{Z_{\rm id}}\frac{\delta Z_{\rm id}}{\delta W_\alpha(\mathbf{r})} \\ &= \frac{-1}{Z_{\rm id}}\frac{\delta}{\delta W_\alpha(\mathbf{r})}\int \mathcal{D}\mathbf{r}\ \exp\left\{-U_{\rm id} - \sum_{i=1}^{M}\int d^3r\ W_\alpha(\mathbf{r})C_\alpha(\mathbf{r})\right\} \\ &= \frac{1}{Z_{\rm id}}\int \mathcal{D}\mathbf{r}\ C_\alpha(\mathbf{r})\exp\left\{-U_{\rm id} + H_{\rm c}\right\} \\ &= \langle C_\alpha(\mathbf{r})\rangle_{\rm id} = \Phi_\alpha(\mathbf{r})/v \quad . \end{aligned} \tag{17}$$

A straightforward evaluation of $\delta H_{\rm f}/\delta\Omega_\alpha$ yields

$$\frac{\delta H_{\rm f}}{\delta \Omega_\alpha(\mathbf{r})} = -\frac{M}{v\lambda_\alpha}\Omega_\alpha(\mathbf{r}) \tag{18}$$

for $\alpha = 1, \ldots, M-1$, and

$$\frac{\delta H_{\rm f}}{\delta \Omega_M(\mathbf{r})} = -c_0 \tag{19}$$

for $\alpha = M$. The resulting functional derivatives of $H = H_{\rm f} - \ln Z_{\rm id}$ are

$$D_\alpha(\mathbf{r}) = \frac{1}{v}\left[-\frac{M\Omega_\alpha(\mathbf{r})}{\lambda_\alpha} + \Phi_\alpha(\mathbf{r})\right] \tag{20}$$

for all $\alpha < M$, with $\Omega_\alpha(\mathbf{r}) = W_\alpha(\mathbf{r}) - S_\alpha + Y_\alpha(\mathbf{r})$, and

$$D_M(\mathbf{r}) = \frac{1}{v}\left[\Phi_M(\mathbf{r}) - 1\right] \tag{21}$$

for $\alpha = M$.

Saddle-Points and SCF Equations

A saddle-point point of the functional integral is a field configuration for which

$$D_\alpha(\mathbf{r}) = 0 \tag{22}$$

for all $\alpha = 1, \ldots, M$ and all $\mathbf{r}$. The saddle-point condition for $\alpha = M$ is a mean-field version of the incompressibility constraint, which requires that $\langle C_M(\mathbf{r})\rangle_{\rm id} = c_0$ or $\Phi_M(\mathbf{r}) = 1$.

We now show that the saddle point conditions given above are equivalent to the usual self-consistent field (SCF) equations for an incompressible system. The standard formulation of these SCF equations, expressed in terms of volume fraction fields $\phi_1, \ldots, \phi_M$, require that

$$0 = w_i(\mathbf{r}) - \chi_{ij}\phi_j(\mathbf{r}) - e_i\xi(\mathbf{r}) + y_i(\mathbf{r}) \quad , \tag{23}$$

for all $i = 1, \ldots, M$. Here, $\xi(\mathbf{r})$ is a Lagrange multiplier field whose value must be chosen to as to satisfy the incompressibility constraint,

$$1 = e_i\phi_i(\mathbf{r}) \quad . \tag{24}$$

Here and throughout this document, we use Einstein convention for summation over repeated

monomer type indices.

By multiplying Eq. (23) by $v_{\alpha i}$ for any $\alpha < M$ and summing with respect to i, we obtain

$$\begin{aligned} 0 &= v_{\alpha i}\left\{w_i(\mathbf{r}) + y_i(\mathbf{r}) - \chi_{ij}\phi_j(\mathbf{r}) - e_i\xi(\mathbf{r})\right\} \\ &= M[W_\alpha(\mathbf{r}) + Y_\alpha(\mathbf{r})] - v_{\alpha i}P_{ij}\chi_{jk}\phi_k(\mathbf{r}) \quad , \end{aligned} \tag{25}$$

where we have used the facts that $v_{\alpha i}e_i = 0$ and $v_{\alpha k} = v_{\alpha i}P_{ik}$ for $\alpha < M$. We then note that, for states that also satisfy the constraint $e_i\phi_i = 1$,

$$\begin{aligned} v_{\alpha i}P_{ij}\chi_{jk}\phi_k(\mathbf{r}) &= v_{\alpha i}P_{ij}\chi_{jk}\left[P_{kl}\phi_l(\mathbf{r}) + \frac{1}{M}e_k\right] \\ &= v_{\alpha i}\tilde{\chi}_{ij}\phi_j(\mathbf{r}) + v_{\alpha i}\chi_{ij}e_j/M \\ &= \lambda_\alpha v_{\alpha j}\phi_j(\mathbf{r}) + MS_\alpha \end{aligned} \tag{26}$$

where we have used the fact that $v_{\alpha i}\tilde{\chi}_{ij} = \lambda_\alpha v_{\alpha j}$ because $\mathbf{v}_\alpha$ is an eigenvector of the symmetric matrix $\tilde{\boldsymbol{\chi}}$. Substituting back into Eq. (25), while noting that $\Phi_\alpha(\mathbf{r}) = v_{\alpha j}\phi_j(\mathbf{r})$, yields

$$0 = M[W_\alpha(\mathbf{r}) + Y_\alpha(\mathbf{r}) - S_\alpha] - \lambda_\alpha\Phi_\alpha(\mathbf{r}) \quad . \tag{27}$$

Dividing by $-v\lambda_\alpha$ and noting that $\Omega_\alpha(\mathbf{r}) = W_\alpha(\mathbf{r}) + Y_\alpha(\mathbf{r}) - S_\alpha$ then yields

$$0 = \frac{1}{v}\left[-\frac{M\Omega_\alpha(\mathbf{r})}{\lambda_\alpha} + \Phi_\alpha(\mathbf{r})\right] = D_\alpha(\mathbf{r}) \tag{28}$$

in which the second equality follows from Eq. (20). The conventional SCF equations of Eq. (23) thus imply that $D_\alpha(\mathbf{r}) = 0$ for all $\alpha < M$, while the SCF incompressibility constraint is equivalent to a requirement that $D_M(\mathbf{r}) = 0$.

SCFT Free Energy

The SCFT approximation for the free energy, denoted here by A, is given by

$$A = A_{\rm id} + A_{\rm int} + A_{\rm ext} \tag{29}$$

in which

$$\begin{aligned} A_{\rm id} &= -\ln Z_{\rm id} - \frac{1}{v}\int d\mathbf{r}\; w_i(\mathbf{r})\phi_i(\mathbf{r}) \\ A_{\rm int} &= \frac{1}{2v}\int d\mathbf{r}\; \phi_i(\mathbf{r})\chi_{ij}\phi_j(\mathbf{r}) \\ A_{\rm ext} &= -\frac{1}{v}\int d\mathbf{r}\; y_i(\mathbf{r})\phi_i(\mathbf{r}) \quad . \end{aligned} \tag{30}$$

Expanding $\phi_i(\mathbf{r})$ in a basis of eigenvectors yields

$$\begin{aligned} A_{\rm id} &= -\ln Z_{\rm id} - \frac{1}{v}\int d\mathbf{r} \sum_{\alpha=1}^{M} W_\alpha \Phi_\alpha \\ A_{\rm int} &= \frac{1}{v}\int d\mathbf{r}\; \left\{ \sum_{\alpha=1}^{M-1} \left[\frac{1}{2M}\lambda_\alpha \Phi_\alpha^2 + S_\alpha \Phi_\alpha \right] + \frac{1}{2} S_M \right\} \quad , \\ A_{\rm ext} &= -\frac{1}{v}\int d\mathbf{r} \sum_{\alpha=1}^{M} Y_\alpha(\mathbf{r})\Phi_\alpha(\mathbf{r}) \quad . \end{aligned} \tag{31}$$

Using the saddle-point equation $W_\alpha = \lambda_\alpha \Phi_\alpha / M + S_\alpha - Y_\alpha$ for $\alpha < M$ and assuming the validity of the SCF incompressibility constraint $\Phi_M(\mathbf{r}) = 1$ when computing $A_{\rm id}$ yields

$$A_{\rm id} = -\ln Z_{\rm id} - \frac{1}{v}\int d\mathbf{r}\; \left\{ \sum_{\alpha=1}^{M-1} \left(\frac{1}{M}\lambda_\alpha \Phi_\alpha^2 + S_\alpha \Phi_\alpha - Y_\alpha \Phi_\alpha \right) + W_M \right\} \quad . \tag{32}$$

Combining expressions yields a total free energy

$$A = -\ln Z_{\rm id} + \frac{1}{v}\int d\mathbf{r}\; \left\{ -\frac{1}{2M} \sum_{\alpha=1}^{M-1} \lambda_\alpha \Phi_\alpha^2 - W_M - Y_M + \frac{1}{2} S_M \right\} \quad . \tag{33}$$

Again applying the saddle point condition to write $\Phi_\alpha = M(W_\alpha + Y_\alpha - S_\alpha)/\lambda_\alpha$ then yields a saddle-point free energy

$$A = -\ln Z_{\rm id} + \frac{1}{v}\int d\mathbf{r}\,\left\{ -\sum_{\alpha=1}^{M-1} \frac{M(W_\alpha + Y_\alpha - S_\alpha)^2}{2\lambda_\alpha} - W_M - Y_M + \frac{1}{2}S_M \right\} \quad . \tag{34}$$

This is equivalent to the expression for the field theoretic Hamiltonian H given in Eqs. (8) and (9). The value of H at a saddle-point is thus exactly equal to the SCFT free energy given in Eqs. (29) and (30).

Correlation Functions

We now consider the calculation of correlation functions from the results of a field theoretic simulation of an incompressible model. The derivation given here uses differentiation of $Z[Y]$ with respect to the source fields $Y_1, \ldots, Y_M$

Changing Integration Variables

To simplify evaluation of derivatives with respect to the source fields, it is convenient to introduce fields $\psi_1(\mathbf{r}), \ldots, \psi_M(\mathbf{r})$ that are defined by the relations

$$W_\alpha(\mathbf{r}) = \sigma_\alpha \psi_\alpha(\mathbf{r}) \tag{35}$$

for $\alpha = 1, \ldots, M$. This yields $\Omega_\alpha(\mathbf{r}) = \sigma_\alpha\psi_\alpha(\mathbf{r}) + Y_\alpha(\mathbf{r}) - S_\alpha$ for $\alpha = 1, \ldots, M-1$, and $\psi_M(\mathbf{r}) = \omega_M(\mathbf{r})$. We then deform the integral used to compute Z by taking $\psi_1(\mathbf{r}), \ldots, \psi_M(\mathbf{r})$ to be real fields and expressing Z as an integral

$$Z = N^{-1}\int \mathcal{D}\psi\; e^{-H} \tag{36}$$

over these fields. This rewriting of the integral is equivalent to a shift in the integration contour for $\Omega_\alpha(\mathbf{r})$ for fields for which $\alpha < M$ and $\sigma_\alpha = i$ by a real amount $Y_\alpha(\mathbf{r}) - S_\alpha$ so as to obtain an integration contour for $W_\alpha(\mathbf{r})$ that follows the imaginary axis, rather than the contour along which $\Omega_\alpha(\mathbf{r})$ is imaginary used in the original formulation. Because H is an analytic functional, this contour deformation does not change the value of the integral. Expressing H_f as an explicit function of the real ψ fields yields a contribution

$$H_\mathrm{f} = \int d^3r \left\{ -\sum_{\alpha=1}^{M-1} \frac{M[\sigma_\alpha\psi_\alpha + Y_\alpha - S_\alpha]^2}{2v\lambda_\alpha} - i\psi_M c_0 \right\} \quad . \tag{37}$$

In this re-formulation, at fixed values of the fields $\psi_1, \ldots, \psi_M$, H_f thus depends explicitly on the source fields $Y_1, \ldots, Y_{M-1}$, but the W fields that appear in the definition of Z_id instead become independent of the source fields. This change of variables simplifies evaluation of functional derivatives of H with respect to $Y(\mathbf{r})$

Moments and Functional Derivatives

By starting from the original representation of $Z[Y]$ as a configurational integral, it is straightforward to show that the first and second moments of the concentration components $C_1(\mathbf{r}), \ldots, C_M(\mathbf{r})$ can be expressed as functional derivatives

$$\langle C_\alpha(\mathbf{r})\rangle = \frac{1}{Z}\frac{\delta Z}{\delta Y_\alpha(\mathbf{r})} \tag{38}$$

$$\langle C_\alpha(\mathbf{r})C_\beta(\mathbf{r}')\rangle = \frac{1}{Z}\frac{\delta Z[Y]}{\delta Y_\alpha(\mathbf{r})\delta Y_\beta(\mathbf{r}')} \quad . \tag{39}$$

Using the functional integral representation of Z obtained above, the required derivatives of $Z[Y]$ can then be expressed as average values

$$\langle C_\alpha(\mathbf{r})\rangle = \left\langle \frac{\delta H}{\delta Y_\alpha(\mathbf{r})} \right\rangle \tag{40}$$

$$\langle C_\alpha(\mathbf{r})C_\beta(\mathbf{r}')\rangle = \left\langle \frac{\delta H}{\delta Y_\alpha(\mathbf{r})}\frac{\delta H}{\delta Y_\beta(\mathbf{r}')} - \frac{\delta^2 H}{\delta Y_\alpha(\mathbf{r})\,\delta Y_\beta(\mathbf{r}')} \right\rangle \quad , \tag{41}$$

in which the averages on the right-hand-side of each equation represent averages over fields $\psi_1, \ldots, \psi_M$, and in which the functional derivatives of H are evaluated at fixed values of the ψ fields. The required derivatives of H are

$$\begin{aligned} \left.\frac{\delta H}{\delta Y_\alpha(\mathbf{r})}\right|_\psi &= -\frac{M}{v\lambda_\alpha}\Omega_\alpha(\mathbf{r}) \\ \left.\frac{\delta^2 H}{\delta Y_\alpha(\mathbf{r})\,\delta Y_\beta(\mathbf{r}')}\right|_\psi &= -\frac{M}{v\lambda_\alpha}\left.\frac{\delta\Omega_\alpha(\mathbf{r})}{\delta Y_\beta(\mathbf{r}')}\right|_\psi = -\frac{M}{v\lambda_\alpha}\delta_{\alpha\beta}\delta(\mathbf{r}-\mathbf{r}') \quad , \end{aligned} \tag{42}$$

thus giving

$$\langle C_\alpha(\mathbf{r})\rangle = -\frac{M}{v\lambda_\alpha}\langle\Omega_\alpha(\mathbf{r})\rangle \tag{43}$$

$$\langle C_\alpha(\mathbf{r})C_\beta(\mathbf{r}')\rangle = \frac{M^2}{v^2\lambda_\alpha\lambda_\beta}\langle\Omega_\alpha(\mathbf{r})\Omega_\beta(\mathbf{r}')\rangle - \frac{M}{v\lambda_\alpha}\delta_{\alpha\beta}\delta(\mathbf{r}-\mathbf{r}') \quad . \tag{44}$$

By combining these expressions for the first and second moments, one may easily show that

$$\langle\delta C_\alpha(\mathbf{r})\delta C_\beta(\mathbf{r}')\rangle = \frac{M^2}{v^2\lambda_\alpha\lambda_\beta}\langle\delta\Omega_\alpha(\mathbf{r})\delta\Omega_\beta(\mathbf{r}')\rangle - \frac{M}{v\lambda_\alpha}\delta_{\alpha\beta}\delta(\mathbf{r}-\mathbf{r}') \quad , \tag{45}$$

Here and hereafter, we use the notation $\delta f(\mathbf{r})$ to indicate a deviation $\delta f(\mathbf{r}) = f(\mathbf{r}) - \langle f(\mathbf{r})\rangle$ of field f from its average, so that $\delta C_\alpha(\mathbf{r}) = C_\alpha(\mathbf{r}) - \langle C_\alpha(\mathbf{r})\rangle$ and $\delta\Omega_\alpha(\mathbf{r}) = \Omega_\alpha(\mathbf{r}) - \langle\Omega_\alpha(\mathbf{r})\rangle$. Note that, because $\Omega_\alpha = W_\alpha + S_\alpha - Y_\alpha$, while S_α is a constant,

$$\delta\Omega_\alpha(\mathbf{r}) = \delta W_\alpha(\mathbf{r}) - \delta Y_\alpha(\mathbf{r}) \quad . \tag{46}$$

For the special case of a homogeneous liquid in which $\delta Y_\alpha(\mathbf{r}) = 0$ for all α and all $\mathbf{r}$, we thus obtain

$$\langle\delta C_\alpha(\mathbf{r})\delta C_\beta(\mathbf{r}')\rangle = \frac{M^2}{v^2\lambda_\alpha\lambda_\beta}\langle\delta W_\alpha(\mathbf{r})\delta W_\beta(\mathbf{r}')\rangle - \frac{M}{v\lambda_\alpha}\delta_{\alpha\beta}\delta(\mathbf{r}-\mathbf{r}') \tag{47}$$

for all $\alpha, \beta = 1, \ldots, M$. In an incompressible model, however, $\delta C_M(\mathbf{r}) = 0$, and nonzero values of $\langle\delta C_\alpha(\mathbf{r})\delta C_\beta(\mathbf{r}')\rangle$ are obtained only for $\alpha, \beta = 1, \ldots, M-1$.

Structure Factor

Consider the calculation of the structure function in a homogeneous state with $Y_\alpha(\mathbf{r}) = 0$ for all α and $\mathbf{r}$. Let $S_{ij}(\mathbf{k})$ denote the structure function

$$\begin{aligned} S_{ij}(\mathbf{k}) &\equiv \frac{1}{V}\int d\mathbf{r}\int d\mathbf{r}' e^{-i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')}\langle \delta c_i(\mathbf{r})\delta c_j(\mathbf{r}')\rangle \\ &= \frac{1}{V}\langle \hat{c}_i(\mathbf{k})\hat{c}_j(-\mathbf{k})\rangle \quad , \end{aligned} \tag{48}$$

where $\mathbf{k}$ is a wavevevector and $\delta\hat{c}_i(\mathbf{k})$ denotes the Fourier transform of $\delta c_i(\mathbf{r})$ at wavevector $\mathbf{k}$. Here and hereafter, we use carets to denote Fourier transforms of fields, defined using the convention

$$\hat{f}(\mathbf{k}) = \int d\mathbf{r}\; e^{-i\mathbf{k}\cdot\mathbf{r}} f(\mathbf{r}) \quad , \tag{49}$$

The quantity $S_{ij}(\mathbf{k})$ can be expressed in terms of the components of concentration in an eigenvector basis as an expansion

$$S_{ij}(\mathbf{k}) = \frac{1}{VM^2}\sum_{\alpha,\beta=1}^{M-1}\langle \delta\hat{C}_\alpha(\mathbf{k})\delta\hat{C}_\beta(-\mathbf{k})\rangle v_{\alpha i}v_{\beta j} \tag{50}$$

in which $\delta\hat{C}_\alpha(\mathbf{k})$ is the Fourier transform of $\delta C_\alpha(\mathbf{r})$. By evaluating the Fourier transform of Eq. (47), we thus find that

$$S_{ij}(\mathbf{k}) = \sum_{\alpha\beta=1}^{M-1} v_{\alpha i}v_{\beta j}\left\{\frac{1}{v^2\lambda_\alpha\lambda_\beta}G_{\alpha\beta}(\mathbf{k}) - \frac{1}{vM\lambda_\alpha}\delta_{\alpha\beta}\right\} \quad , \tag{51}$$

where

$$G_{ij}(\mathbf{k}) = \frac{1}{V}\langle \delta\hat{W}_\alpha(\mathbf{k})\delta\hat{W}_\beta(-\mathbf{k})\rangle \quad , \tag{52}$$

and where $\delta\hat{W}_\alpha(\mathbf{k})$ is the Fourier transform of $\delta W_\alpha(\mathbf{r})$.

Three Monomer (ABC) Systems

This section provides details of the analysis of three-monomer systems that is summarized in section 4 of the associated article.

Eigenvalues of $\tilde{\boldsymbol{\chi}}$

Consider the calculation of the eigenvalues of a projected χ matrix

$$\tilde{\boldsymbol{\chi}} = \mathbf{P}\boldsymbol{\chi}\mathbf{P} \quad . \tag{53}$$

Here $\mathbf{P} = \mathbf{I} - \mathbf{e}\mathbf{e}^T/M$ is a projection matrix, and $\boldsymbol{\chi}$ is a symmetric matrix of Flory-Huggins χ parameters. From simplicity, we consider the conventional choice of a χ matrix with vanishing diagonal elements, of the form

$$\boldsymbol{\chi} = \begin{bmatrix} 0 & \chi_{12} & \chi_{13} \\ \chi_{12} & 0 & \chi_{23} \\ \chi_{13} & \chi_{23} & 0 \end{bmatrix} \quad , \tag{54}$$

with $\chi_{11} = \chi_{22} = \chi_{33} = 0$.

The projected matrix $\tilde{\boldsymbol{\chi}} = \mathbf{P}\boldsymbol{\chi}\mathbf{P}$ is a singular matrix for which $\tilde{\boldsymbol{\chi}}\mathbf{e} = 0$, because $\mathbf{P}\mathbf{e} = 0$. By construction, $\tilde{\boldsymbol{\chi}}$ thus must have one zero eigenvalue with an associated eigenvector $\mathbf{e}$. To isolate the two remaining nontrivial eigenvalues, we first apply an orthogonal transformation of this matrix that reduces it to a block diagonal form in which the remaining nonzero elements form a 2×2 matrix. Let $\mathbf{A}$ denote a transformed matrix

$$\mathbf{A} = \mathbf{U}^T\tilde{\boldsymbol{\chi}}\mathbf{U} \tag{55}$$

in which $\mathbf{U}$ is a a real orthogonal matrix with orthonormal columns $\mathbf{u}_1$, $\mathbf{u}_2$, and $\mathbf{u}_3$. Each

element of $\mathbf{A}$ can be expressed as a matrix product

$$A_{ij} = \mathbf{u}_i^T \tilde{\boldsymbol{\chi}} \mathbf{u}_j = \mathbf{u}_i^T \mathbf{P} \tilde{\boldsymbol{\chi}} \mathbf{P} \mathbf{u}_j \tag{56}$$

for $i, j = 1, \ldots, 3$.

Because $\mathbf{e}$ is always an eigenvector of $\tilde{\boldsymbol{\chi}}$, $\mathbf{A}$ can be transformed to a block diagonal form by taking the last basis vector $\mathbf{u}_3$ to be a normalized vector proportional to $\mathbf{e}$. We thus take

$$\mathbf{u}_3 = \mathbf{e}/\sqrt{3} \quad , \tag{57}$$

for which $\mathbf{u}_3^T \mathbf{u}_3 = 1$. Because $\tilde{\boldsymbol{\chi}} \mathbf{e} = 0$, and $\tilde{\boldsymbol{\chi}}^T = \tilde{\boldsymbol{\chi}}$, use of this choice in Eq. (56) yields $A_{ij} = 0$ for all elements with $i = 3$ or $j = 3$. This choice is thus guaranteed to yield a matrix $\mathbf{A}$ in which all elements of the last row and last column are zero.

A transformation of this form thus leaves a matrix in which the remaining nonzero elements form an upper-left 2×2 submatrix. Let $\mathbf{B}$ denote this submatrix. Because the unspecified basis vectors $\mathbf{u}_1$ and $\mathbf{u}_2$ must both be orthogonal to $\mathbf{e}$, they must both satisfy $\mathbf{P}\mathbf{u}_i = \mathbf{u}_i$. Using this to further simplify Eq. (56) for the remaining elements of $\mathbf{A}$, we find that

$$B_{ij} = A_{ij} = \mathbf{u}_i^T \tilde{\boldsymbol{\chi}} \mathbf{u}_j = \mathbf{u}_i^T \boldsymbol{\chi} \mathbf{u}_j \tag{58}$$

for $i, j \in \{1, 2\}$.

The two eigenvalues of the remaining 2×2 matrix $\mathbf{B}$ are independent of our choice of valid pair of orthonormal basis vectors $\mathbf{u}_1$ and $\mathbf{u}_2$. The calculation presented here uses the specific choice

$$\mathbf{u}_1 = \frac{1}{\sqrt{6}} \begin{bmatrix} 1 \\ -2 \\ 1 \end{bmatrix} \qquad \mathbf{u}_2 = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ 0 \\ -1 \end{bmatrix} \quad . \tag{59}$$

Using these basis vectors in Eq. (58) for a χ matrix with vanishing diagonal elements yields

a 2×2 matrix

$$\mathbf{B} = \begin{bmatrix} (\chi_{13} - 2\chi_{12} - 2\chi_{23})/3 & (\chi_{23} - \chi_{12})/\sqrt{3} \\ (\chi_{23} - \chi_{12})/\sqrt{3} & -\chi_{13} \end{bmatrix} \quad . \tag{60}$$

A straightforward calculation of the determinant of this matrix yields

$$|\mathbf{B}| = [2J - K]/3 \tag{61}$$

where J and K are the permutation invariants

$$\begin{aligned} J &= \chi_{12}\chi_{13} + \chi_{12}\chi_{23} + \chi_{13}\chi_{23} \\ K &= \chi_{12}^2 + \chi_{23}^2 + \chi_{13}^2 \quad . \end{aligned} \tag{62}$$

Eigenvalues of $\mathbf{B}$ may be computed by requiring that $|\mathbf{I}\lambda - \mathbf{B}| = 0$, which yields a quadratic equation for λ. The two roots of the resulting quadratic yield eigenvalues

$$\lambda_\pm = \frac{1}{3}\left[-L \pm 2\sqrt{K - J}\right] \quad , \tag{63}$$

in which

$$L = \chi_{12} + \chi_{23} + \chi_{13} \quad . \tag{64}$$

Using the identity $L^2 = K + 2J$, it is straightforward to confirm that the product $\lambda_+\lambda_-$ yields the expected determinant,

$$\lambda_+\lambda_- = |\mathbf{B}| = (2J - K)/3 \quad . \tag{65}$$

Hildebrand Approximation

The Hildebrand approximation for interaction parameters in mixtures of simple non-polar monomer types with dispersion interactions requires that

$$\chi_{ij} = v(\delta_i - \delta_j)^2/kT \tag{66}$$

where δ_i is a "solubility parameter" characteristic of a homopolymer containing monomomers of type i. The ordering monomer type indices is arbitrary, and so we may choose indices such that $\delta_1 < \delta_2 < \delta_3$ without loss of generality. With this convention, we may then parameters Δ, α and β such that

$$\begin{aligned} \delta_3 - \delta_1 &= \Delta \\ \delta_2 - \delta_1 &= \alpha\Delta \\ \delta_3 - \delta_2 &= \beta\Delta \quad , \end{aligned} \tag{67}$$

with $\alpha, \beta \in [0, 1]$ and $\alpha + \beta = 1$. This parameterization yields $\chi_{12} = \alpha^2\chi_{13}$ and $\chi_{23} = \beta^2\chi_{13}$. A straightforward substitution yields permutation invariants

$$\begin{aligned} J &= \chi_{13}^2(\alpha^2 + \alpha^2\beta^2 + \beta^2) \\ K &= \chi_{13}^2(1 + \alpha^4 + \beta^4) \\ L &= \chi_{13}(1 + \alpha^2 + \beta^2) \quad . \end{aligned} \tag{68}$$

To show the relationship among these expressions more clearly, we need the identities

$$\begin{aligned} 1 &= (\alpha + \beta)^2 = \alpha^2 + \beta^2 + 2\alpha\beta \\ 1 &= (\alpha + \beta)^4 = \alpha^4 + \beta^4 + 4(\alpha^3\beta + \alpha\beta^3) + 6\alpha^2\beta^2 \\ &= \alpha^4 + \beta^4 + 4\alpha\beta(1 - 2\alpha\beta) + 6\alpha^2\beta^2 \end{aligned}$$

$$= \quad \alpha^4 + \beta^4 + 4\alpha\beta - 2\alpha^2\beta^2 \quad . \tag{69}$$

Using these identities to replace the quantities $\alpha^2 + \beta^2$ and $\alpha^4 + \beta^4$ with polynomials of $\alpha\beta$, we find that

$$K = 2J = \chi_{13}^2 2(1 - 2\alpha\beta + \alpha^2\beta^2) \quad . \tag{70}$$

Because this yields $K = 2J$, while $\lambda_-\lambda_+ = (2J - K)/3$ by Eq. (65), Eq. (70) implies

$$\lambda_-\lambda_+ = 0 \tag{71}$$

in the Hildebrand approximation for arbitrary value of the parameters Δ and α. For any $\Delta > 0$, $L > 0$ by Eq. (68), and so $\lambda_- < 0$ by Eq. (63), implying that $\lambda_+ = 0$.

Weakly Compressible Model

This section presents some details of the analysis of the weakly compressible model that is discussed in section 5 of the associated article. The first Subsection summarizes the definition of the model and corresponding field theoretic Hamiltonian. The remaining two subsections analyze the behavior of the eigenvalues and eigenvectors of the matrix $\mathbf{U}$ in the limit of a very large dimensionless compression modulus parameter ζ. The last subsection establishes the sense in which the incompressible limit of the compressible model is asymptotically equivalent to the incompressible model.

Working Equations

We first recap some of the working equations for the compressible model, as given in Section 6 in the associated article. We consider a model with M monomer types with concentrations

$c_1, \ldots, c_M$, with a potential energy

$$\begin{aligned} U &= U_{\rm int} + U_{\rm ext} \\ U_{\rm int} &= \int d\mathbf{r} \left\{ \frac{v}{2} U_{ij} c_i c_j - \zeta e_i c_i \right\} + U_{\rm int}^{(0)} \quad , \qquad (72) \\ U_{\rm ext} &= -\int d\mathbf{r}\; y_i c_i \qquad (73) \end{aligned}$$

in which U_{ij} is an element of an $M \times M$ matrix

$$\mathbf{U} = \boldsymbol{\chi} + \boldsymbol{\zeta} \mathbf{e} \mathbf{e}^{\boldsymbol{T}} \quad , \qquad (74)$$

while $U_{\rm int}^{(0)} = \zeta V c_0/2$. The fields $y_1(\mathbf{r}), \ldots, y_M(\mathbf{r})$ are externally imposed source fields.

For all $\alpha = 1, \ldots, M$, $\mathbf{x}_\alpha$ and κ_α denote an eigenvector and associated eigenvalue of $\mathbf{U}$, respectively, such that

$$\mathbf{U}\mathbf{x}_\alpha = \kappa_\alpha \mathbf{x}_\alpha \qquad (75)$$

for all $\alpha = 1, \ldots, M$, with a normalization $\mathbf{x}_\alpha^T \mathbf{x}_\beta = \delta_{\alpha\beta} M$. Because $\mathbf{U}$ is real and symmetric, these eigenvalues and eigenvectors are real. For each $\alpha = 1, \ldots, M$, let $\sigma_\alpha = 1$ if $\kappa_\alpha < 0$ and let $\sigma_\alpha = i$ if $\kappa_\alpha > 0$. We consider the limit of large positive values of ζ, and take λ_M to be the largest eigenvalue, which will be shown to increase linearly with increasing ζ.

Applying a Hubbard-Stratonovich transformation, by introducing auxiliary fields $\psi_1, \ldots, \psi_M$, yields an expression for the partition function Z as a functional integral with a field-theoretic Hamiltonian

$$\begin{aligned} H[\psi] &= -\ln Z_{\rm id} + H_{\rm f} \\ H_{\rm f} &= \sum_{\alpha=1}^{M} \int d\mathbf{r} \frac{M \psi_\alpha^2}{2v|\kappa_\alpha|} + U_{\rm int}^{(0)} \qquad (76) \end{aligned}$$

in which $Z_{\rm id}[W]$ is the partition function of an ideal gas that is subjected to an applied

potential

$$H_c = \sum_{\alpha=1}^{M} W_\alpha(\mathbf{r}) C_\alpha(\mathbf{r}) \quad , \tag{77}$$

where

$$W_\alpha(\mathbf{r}) = \Psi_\alpha(\mathbf{r}) - \zeta E_\alpha - Y_\alpha \quad , \tag{78}$$

$$\Psi_\alpha(\mathbf{r}) = \sigma_\alpha \psi_\alpha(\mathbf{r}) \quad , \tag{79}$$

while

$$E_\alpha \equiv \mathbf{x}_\alpha^T \mathbf{e}/M \qquad Y_\alpha(\mathbf{r}) \equiv \mathbf{x}_\alpha^T \mathbf{y}_i(\mathbf{r})/M \tag{80}$$

denote components of the vectors $\mathbf{e}$ and $\mathbf{y} = [y_1, \ldots, y_M]^T$ in a basis of eigenvectors.

Limits of Eigenvectors and Eigenvalues

We consider the behavior of the eigenvectors and eigenvalues of $\mathbf{U}$ in a limit in which we take $\zeta \to \infty$ while holding the elements of the χ matrix constant. To describe this limit, it is useful to consider the corresponding eigenvectors and eigenvalues of a scaled matrix

$$\mathbf{A} \equiv \mathbf{U}/\zeta = \mathbf{e}\mathbf{e}^T + \boldsymbol{\chi}/\zeta \quad . \tag{81}$$

Every eigenvector $\mathbf{x}_\alpha$ of $\mathbf{U}$ is also an eigenvector of $\mathbf{A}$ with an eigenvalue that we denote by a_α, such that

$$\mathbf{A}\mathbf{x}_\alpha = a_\alpha \mathbf{x}_\alpha \qquad a_\alpha = \kappa_\alpha/\zeta \tag{82}$$

for each $\alpha = 1, \ldots, M$. Let $\mathbf{x}_\alpha^{(0)}$ and $\mathbf{a}_\alpha^{(0)}$ denote the limiting values of eigenvector $\mathbf{x}_\alpha$ and eigenvalue a_α, respectively, such that

$$\mathbf{x}_\alpha^{(0)} = \lim_{\zeta\to\infty} \mathbf{x}_\alpha \quad , \tag{83}$$

$$a_\alpha^{(0)} = \lim_{\zeta\to\infty} a_\alpha \quad . \tag{84}$$

for $\alpha = 1, \ldots, M$, where the limits are evaluated at fixed χ.

Observe that the matrix $\mathbf{A}$ approaches a limit

$$\lim_{\zeta \to \infty} \mathbf{A} = \mathbf{e}\mathbf{e}^T \tag{85}$$

as $\zeta \to \infty$. This implies that

$$\mathbf{e}\mathbf{e}^T \mathbf{x}_\alpha^{(0)} = \mathbf{x}_\alpha^{(0)} a_\alpha^{(0)} \tag{86}$$

for all $\alpha = 1, \ldots, M$. The limiting matrix $\mathbf{e}\mathbf{e}^T$ has one eigenvector equal to $\mathbf{e}$ with an associated eigenvalue M, and a $M-1$ dimensional eigenspace of all vectors that are orthogonal to $\mathbf{e}$ with an associated eigenvalue of zero. In the limit $\zeta \to \infty$, $\mathbf{A}$ must thus have one eigenvector that approaches $\mathbf{e}$ for which $a_\alpha^{(0)} = M$, and $M-1$ eigenvectors that are orthogonal to $\mathbf{e}$ for which $a_\alpha^{(0)} = 0$. By convention, we assign an index M to the eigenvector that approaches $\mathbf{e}$, for which $a_M \to M$, and assign indices $\alpha = 1, \ldots, M-1$ to the $M-1$ eigenvectors for which $a_\alpha \to 0$. With this convention, we obtain

$$\mathbf{x}_M^{(0)} = \mathbf{e} \qquad a_M^{(0)} = M \tag{87}$$

while $\mathbf{e}^T \mathbf{x}_\alpha^{(0)} = 0$ and $a_\alpha^{(0)} = 0$ for all $\alpha < M$.

To identify the limits of the remaining $M-1$ eigenvectors and eigenvalues of $\mathbf{U}$, we start from the original eigenvalue equation $\mathbf{U}\mathbf{x}_\alpha = \lambda_\alpha \mathbf{x}_\alpha$ for any $\alpha < M$. Multiplying this eigenvalue equation from the left by the projection operator $\mathbf{P}$ and taking the limit $\zeta \to \infty$ yields

$$\lim_{\zeta \to \infty} \mathbf{P}\mathbf{U}\mathbf{x}_\alpha = \lim_{\zeta \to \infty} \kappa_\alpha \mathbf{P}\mathbf{x}_\alpha \quad . \tag{88}$$

We then observe that $\mathbf{P}\mathbf{U} = \mathbf{P}\boldsymbol{\chi}$ for any value of ζ, and that $\mathbf{x}_\alpha^{(0)}$ must be orthogonal to $\mathbf{e}$ for $\alpha < M$, and thus that $\mathbf{x}_\alpha^{(0)} = \mathbf{P}\mathbf{x}_\alpha^{(0)}$. With these simplifications, we find that

$$\mathbf{P}\boldsymbol{\chi}\mathbf{P}\mathbf{x}_\alpha^{(0)} = \tilde{\boldsymbol{\chi}}\mathbf{x}_\alpha^{(0)} = \kappa_\alpha^{(0)}\mathbf{x}_\alpha^{(0)} \tag{89}$$

for $\alpha < M$, where $\tilde{\boldsymbol{\chi}} = \mathbf{P}\boldsymbol{\chi}\mathbf{P}$, and where

$$\kappa_\alpha^{(0)} = \lim_{\zeta\to\infty} \kappa_\alpha = \lim_{\zeta\to\infty} \zeta a_\alpha \quad . \tag{90}$$

The solutions the eigenvalue problem given in Eq. (89) are precisely the $M-1$ nonzero eigenvectors and corresponding eigenvalues of the projected χ matrix, $\tilde{\boldsymbol{\chi}}$. denoted by $\mathbf{v}_1, \ldots, \mathbf{v}_{M-1}$ and $\lambda_1, \ldots, \lambda_{M-1}$, respectively. The limiting values of the remaining $M-1$ eigenvectors and eigenvalues of $\mathbf{U}$ are thus all equal to corresponding nontrivial eigenvectors and eigenvalues of $\tilde{\boldsymbol{\chi}}$, such that

$$\begin{aligned} \mathbf{x}_\alpha^{(0)} &= \mathbf{v}_\alpha \\ \kappa_\alpha^{(0)} &= \lambda_\alpha \end{aligned} \tag{91}$$

for all $\alpha = 1, \ldots, M-1$.

Because $\mathbf{x}_M^{(0)} = \mathbf{e}$, and we also take $\mathbf{v}_M = \mathbf{e}$ by convention, we thereby actually obtain $\mathbf{x}_\alpha^{(0)} = \mathbf{v}_\alpha$ for all $\alpha = 1, \ldots, M$, including $\alpha = M$. To simplify notation, we thus hereafter drop the notation $\mathbf{x}_\alpha^{(0)}$ in favor of $\mathbf{v}_\alpha$. To summarize, in the limit $\zeta \to \infty$:

- Every eigenvector $\mathbf{x}_\alpha$ of $\mathbf{U}$ approaches a corresponding eigenvector $\mathbf{v}_\alpha$ of $\tilde{\boldsymbol{\chi}}$. We index the eigenvectors such that $\mathbf{x}_M \to \mathbf{e}$.
- For $\alpha < M$, each eigenvalue κ_α of $\mathbf{U}$ approaches a corresponding eigenvalue λ_α of $\tilde{\boldsymbol{\chi}}$.
- For $\alpha = M$, $\kappa_M \to \infty$, such that

$$\lim_{\zeta\to\infty} \kappa_M/\zeta = a_M^{(0)} = M \quad . \tag{92}$$

First Order Perturbation Theory

Some aspects of our analysis of the relationship between the compressible and incompressible theories require information about small deviations of the eigenvectors $\mathbf{U}$ from their limiting values in the case of large but finite ζ. To construct an appropriate perturbation theory, we express $\mathbf{A}$ as a sum

$$\mathbf{A} = \mathbf{A}^{(0)} + \mathbf{A}^{(1)} \tag{93}$$

in which

$$\mathbf{A}^{(0)} = \mathbf{e}\mathbf{e}^T \qquad \mathbf{A}^{(1)} = \boldsymbol{\chi}/\zeta \quad . \tag{94}$$

Using this decomposition, we apply a standard Rayleigh-Schrödinger perturbation theory in which $\mathbf{A}^{(0)}$ is treated as the unperturbed matrix and $\mathbf{A}^{(1)}$ is treated as a small perturbation. Because $\mathbf{A}^{(1)}$ is proportional to $1/\zeta$, this naturally yields an expansion in powers of $1/\zeta$. We use a basis of vectors $\mathbf{v}_1, \ldots, \mathbf{v}_M$, which are all eigenvectors of $\mathbf{A}^{(0)}$ with eigenvalues of 0 or 1. For each $\alpha = 1, \ldots, M$, we define an eigenvector $\mathbf{w}_\alpha$ of $\mathbf{A}$ that can be expressed as an expansion

$$\mathbf{w}_\alpha = \mathbf{v}_\alpha + \Delta\mathbf{w}_\alpha \tag{95}$$

in which $\mathbf{v}_\alpha^T \Delta\mathbf{w}_\alpha = 0$. The vector $\mathbf{w}_\alpha$ thus satisfies the so-called "intermediate" normalization condition

$$\mathbf{v}_\alpha^T \mathbf{w}_\alpha = M \quad . \tag{96}$$

The normalized eigenvector $\mathbf{x}_\alpha$ for which $\mathbf{x}_\alpha^T \mathbf{x}_\alpha = M$ is colinear with $\mathbf{w}_\alpha$, and is given by

$$\mathbf{x}_\alpha = \frac{\mathbf{v}_\alpha + \Delta\mathbf{w}_\alpha}{[1 + M^{-1}|\Delta\mathbf{w}_\alpha|^2]^{1/2}} \quad . \tag{97}$$

We also expand each associated eigenvalue of $\mathbf{A}$ as

$$a_\alpha = a_\alpha^{(0)} + \Delta a_\alpha \quad , \tag{98}$$

where Δa_α is a perturbation that vanishes as $\zeta \to \infty$.

We seek solutions of the eigenvalue problem $\mathbf{A}\mathbf{w}_\alpha = a_\alpha \mathbf{w}_\alpha$ or, equivalently,

$$(\mathbf{A}^{(0)} + \mathbf{A}^{(1)})(\mathbf{v}_\alpha + \Delta\mathbf{w}_\alpha) = (a_\alpha^{(0)} + \Delta a_\alpha)(\mathbf{v}_\alpha + \Delta\mathbf{w}_\alpha) \quad . \tag{99}$$

Equating contributions that are of first order in $1/\zeta$ yields

$$[\mathbf{A}^{(0)} - a_\alpha^{(0)}\mathbf{I}]\Delta\mathbf{w}_\alpha + \mathbf{A}^{(1)}\mathbf{v}_\alpha \simeq (\Delta a_\alpha)\mathbf{v}_\alpha \quad . \tag{100}$$

A standard analysis, closely analogous to the standard first order time-independent quantum mechanical perturbation theory, using a perturbation $\mathbf{A}^{(1)} = \boldsymbol{\chi}/\zeta$, yields eigenvalue and eigenvector perturbations

$$\Delta a_\alpha \simeq \frac{1}{\zeta M}\mathbf{v}_\alpha^T \boldsymbol{\chi}\mathbf{v}_\alpha \tag{101}$$

$$\Delta\mathbf{w}_\alpha \simeq \frac{1}{\zeta M}\sum_{\beta\neq\alpha}\mathbf{v}_\beta \frac{\mathbf{v}_\beta^T\boldsymbol{\chi}\mathbf{v}_\alpha}{a_\alpha^{(0)} - a_\beta^{(0)}} \tag{102}$$

to first order in $1/\zeta$.

Applying this formalism to any $\alpha < M$, for which $\mathbf{v}_\alpha = \mathbf{P}\mathbf{v}_\alpha$, yields first order perturbations

$$\Delta a_\alpha \simeq \frac{\lambda_\alpha}{\zeta} \tag{103}$$

$$\Delta\mathbf{w}_\alpha \simeq -\mathbf{e}\frac{S_\alpha}{\zeta} \quad , \tag{104}$$

where $S_\alpha = \mathbf{v}_\alpha^T\boldsymbol{\chi}\mathbf{e}/M^2$ by Eq. (6). Note that, because $a_\alpha^{(0)} = 0$ for all $\alpha < M$, $\Delta a_\alpha = \kappa_\alpha/\zeta$ or, equivalently, $\kappa_\alpha = \zeta\Delta a_\alpha$. Eq. (103) thus implies that $\kappa_\alpha \simeq \lambda_\alpha$ for $\alpha < M$, in agreement with Eq. (91). It is straightforward to show that $\mathbf{w}_\alpha \simeq \mathbf{x}_\alpha$ to $\mathcal{O}(1/\zeta)$, though the colinear vectors $\mathbf{w}_\alpha$ and $\mathbf{x}_\alpha$ differ at order $\mathcal{O}(1/\zeta^2)$ and higher because of differences in normalization

convention. Eq. (104) for $\Delta\mathbf{w}_\alpha$ can thus be used to show that

$$\lim_{\zeta\to\infty} \zeta E_\alpha = \lim_{\zeta\to\infty} \zeta \mathbf{e}^T \mathbf{x}_\alpha / M = -S_\alpha \tag{105}$$

for all $\alpha < M$.

Applying this formalism to $\alpha = M$, for which $\mathbf{v}_M = \mathbf{e}$, yields

$$\Delta a_M \simeq \frac{M S_M}{\zeta} \tag{106}$$

$$\Delta\mathbf{w}_M \simeq \frac{1}{\zeta} \sum_{\alpha=1}^{M-1} \mathbf{v}_\alpha S_\alpha \quad , \tag{107}$$

where $S_\alpha = \mathbf{v}_\alpha^T \boldsymbol{\chi} \mathbf{e}/M^2$ and $S_M = \mathbf{e}^T \boldsymbol{\chi} \mathbf{e}/M^2$. Eq. (106) and the relationship $\Delta a_M = \kappa_M/\zeta - M$ together imply that

$$\lim_{\zeta\to\infty} \frac{\zeta \Delta a_M}{M} = \lim_{\zeta\to\infty} \zeta \left(\frac{\kappa_M}{\zeta M} - 1 \right) = S_M \quad . \tag{108}$$

Using Eq. (107) for $\Delta\mathbf{w}_M$, it is straightforward to show that

$$\lim_{\zeta\to\infty} E_M = 1 \quad . \tag{109}$$

Starting from Eq. (107), we may also show that the deviation $1 - E_M$ decreases as $1/\zeta^2$ with increasing ζ, and thus that

$$\begin{aligned} \lim_{\zeta\to\infty} \zeta(1 - E_M) &= 0 \quad . \\ \lim_{\zeta\to\infty} \zeta(1 - E_M^2) &= 0 \quad . \end{aligned} \tag{110}$$

The limits given in Eq. (105) and Eqs. (108 - 110) are used below to establish asymptotic relationship between values of the Hamiltonian in the compressible and incompressible theories.

The fact that the first $M-1$ eigenvalues of $\mathbf{U}$ approach corresponding eigenvalues of $\tilde{\boldsymbol{\chi}}$, and that $\sigma_M = i$ for both theories, together imply that the value of σ_α for the incompressible theory in the limit $\zeta \to \infty$ is the same as its value in the incompressible theory, for all $\alpha = 1, \ldots, M$,

Asymptotically Equivalent Variables

To establish a closer correspondence between variables in the compressible and incompressible theories, we consider a limiting process in which we take $\zeta \to \infty$ while holding constant all the elements of the χ matrix, the monomer source fields $y_1(\mathbf{r}), \ldots, y_M(\mathbf{r})$ and the monomer chemical potential fields $w_1(\mathbf{r}), \ldots, w_M(\mathbf{r})$. States of the incompressible and compressible theories for which these quantities (the χ matrix, the y fields and the w fields) have equal values are referred to here as "corresponding states". A quantity A that depends upon the field configuration in the compressible theory will be said to "asymptotically equivalent" to a corresponding quantity B that depends on the field configuration in the incompressible theory A approaches a limit as $\zeta \to \infty$ that is equal to the value of B in a corresponding state of the incompressible theory.

The fact that each of the eigenvectors of $\mathbf{U}$ approaches a corresponding eigenvector of $\tilde{\boldsymbol{\chi}}$ as $\zeta \to 0$ immediately implies that the values of $W_\alpha(\mathbf{r})$ and $Y_\alpha(\mathbf{r})$ in the compressible theory are asymptotically equivalent to values of variables of the same names in the incompressible theory, for all $\alpha = 1, \ldots, M$.

Fluctuating Fields

Eqs. (78) and (105) together imply that

$$\lim_{\zeta \to \infty} \Psi_\alpha(\mathbf{r}) = W_\alpha(\mathbf{r}) - S_\alpha + Y_\alpha(\mathbf{r}) = \Omega_\alpha(\mathbf{r}) \tag{111}$$

for all $\alpha < M$, where $\Omega_\alpha(\mathbf{r})$ denotes a value defined in a corresponding state of the incompressible theory, as given by Eq. (13). This demonstrates that Ψ_α is asymptotically equivalent to Ω_α for all $\alpha < M$. Because $\Psi_\alpha = \sigma_\alpha \psi_\alpha$ and $\Omega_\alpha = \sigma_\alpha \omega_\alpha$, this also implies that $\psi_\alpha(\mathbf{r})$ is asymptotically equivalent to $\omega_\alpha(\mathbf{r})$ for $\alpha < M$.

We next consider the relationship between pressure-like fields, Ψ_M in the compressible theory and Ω_M in the incompressible theory. Eq. (78) implies that

$$\Psi_M(\mathbf{r}) - \zeta E_M = \Omega_M(\mathbf{r}) = W_M(\mathbf{r}) + Y_M(\mathbf{r}) \tag{112}$$

for corresponding states of the compressible and incompressible theory, for any value of ζ. Taking the limit $\zeta \to \infty$, and using Eq. (109) for the limit $E_M \to 1$, we find that

$$\lim_{\zeta \to \infty} [\ \Psi_M(\mathbf{r}) - \zeta\ ] = \Omega_M(\mathbf{r}) \quad . \tag{113}$$

We thus find that $\Psi_M - \zeta$ is asymptotically equivalent to Ω_M.

Values of H

To compare values of the Hamiltonian for the compressible and incompressible theories, we first note that the Hamiltonian for each model can be expressed as sum $H = -\ln Z_{\rm id} + H_{\rm f}$, and that values of $\ln Z_{\rm id}$ are equal in corresponding states of the two models. The equivalence of values of $Z_{\rm id}$ in corresponding states follows from the fact that in both theories $Z_{\rm id}$ is a functional of the monomer chemical potential fields $w_1, \ldots, w_M$, and that corresponding states are defined to be states with equal values for these fields. Values of H in the two theories are thus asymptotically equivalent if and only if values of $H_{\rm f}$ are asymptotically equivalent.

To compare values of $H_{\rm f}$ in the two theories, it is convenient to divide $H_{\rm f}$ in each theory into two components, and establish the relationship between corresponding components. For

the compressible model, we express values of $H_{\rm f}$ as a sum

$$\begin{aligned} H_{\rm f}[\Psi] &= A + B \\ A &= -\sum_{\alpha=1}^{M-1} \int d\mathbf{r} \frac{M\Psi_\alpha^2}{2v\kappa_\alpha} \\ B &= \frac{\zeta V}{2v} - \int d\mathbf{r} \frac{M\Psi_M^2}{2v\kappa_M} \quad , \end{aligned} \tag{114}$$

in which $\Psi_\alpha(\mathbf{r}) = \sigma_\alpha \psi_\alpha(\mathbf{r})$. For the incompressible model, we express $H_{\rm f}$ as a sum

$$\begin{aligned} H_{\rm f}[\Omega] &= C + D \\ C &= -\sum_{\alpha=1}^{M-1} \int d\mathbf{r} \frac{M\Omega_\alpha^2}{2v\lambda_\alpha} \\ D &= \frac{S_M V}{2v} - c_0 \int d\mathbf{r}\ \Omega_M(\mathbf{r}) \quad , \end{aligned} \tag{115}$$

in which $\Omega_\alpha(\mathbf{r}) = \sigma_\alpha \omega_\alpha(\mathbf{r})$. In what follows, we demonstrate the asymptotic equivalence of values of $H_{\rm f}$ in the two theories by showing that A is asymptotically equivalent to C, and that B is asymptotically equivalent to D.

The asymptotic equivalence of A and C follows immediately from the fact that $\kappa_\alpha \to \lambda_\alpha$ and $\Psi_\alpha(\mathbf{r}) \to \Omega_\alpha(\mathbf{r})$ for all $\alpha < M$ as $\zeta \to \infty$ in corresponding states of the two theories.

We now consider the relationship between B and D. The incompressible limit of B yields

$$\lim_{\zeta\to\infty} B = \lim_{\zeta\to\infty} \left\{ \frac{\zeta V}{2v} - \int d\mathbf{r} \frac{M(W_M + Y_M + \zeta E_M)^2}{2v\kappa_M} \right\} \tag{116}$$

or

$$\begin{aligned} \lim_{\zeta\to\infty} B &= -\lim_{\zeta\to\infty} \int d\mathbf{r} \frac{M(W_M + Y_M)^2}{2v\kappa_M} \\ &\quad - \lim_{\zeta\to\infty} \frac{M\zeta}{v\kappa_M} E_M \int d\mathbf{r}(W_M + Y_M) \\ &\quad + \frac{V}{2v} \lim_{\zeta\to\infty} \zeta(1 - \frac{M\zeta E_M^2}{\kappa_M}) \quad . \end{aligned} \tag{117}$$

The expression on the first line of the RHS of Eq. (117) vanishes because $1/\kappa_M \to 0$ as $\zeta \to \infty$. The limit of the expression given in the last line of the RHS can be evaluated by using the limits $M\zeta/\kappa_M \to 1$ and Eqs. (108 - 110) to show that

$$\begin{aligned}
\lim_{\zeta\to\infty} \zeta \left(1 - \frac{M\zeta E_M^2}{\kappa_M}\right) &= \lim_{\zeta\to\infty} \zeta \frac{M\zeta}{\kappa_M} \left(\frac{\kappa_M}{M\zeta} - E_M^2\right) \\
&= \lim_{\zeta\to\infty} \frac{M\zeta}{\kappa_M} \zeta \left(\frac{\kappa_M}{M\zeta} - 1\right) + \lim_{\zeta\to\infty} \frac{M\zeta}{\kappa_M} \zeta \left(1 - E_M^2\right) \\
&= S_M \quad . \qquad (118)
\end{aligned}$$

Combining terms, we find that

$$\begin{aligned}
\lim_{\zeta\to\infty} B &= \frac{S_M V}{2v} - c_0 \int d\mathbf{r} \, [\, W_M(\mathbf{r}) + Y_M(\mathbf{r}) \,] \\
&= \frac{S_M V}{2v} - c_0 \int d\mathbf{r} \, \Omega_M(\mathbf{r}) \\
&= D \quad . \qquad (119)
\end{aligned}$$

This demonstates asymptotic equivalence of quantities B and D, which completes the demonstration of the asymptotic equivalence of values of both $H_{\rm f}$ and H in the compressible and incompressible theories.

Functional Derivatives

The asymptotic equivalence of values of H in the compressible and incompressible theories also implies the asymptotic equivalence of expressions for corresponding functional derivatives, as a corollary. We can, however, also more directly confirm the equivalence of explicit expressions for these derivatives.

A straightforward calculation of the derivative $\delta H/\delta\Psi_\alpha$ in the compressible theory yields

$$\frac{\delta H}{\delta \Psi_\alpha(\mathbf{r})} = -\frac{M\Psi_\alpha(\mathbf{r})}{v\kappa_\alpha} + \langle C_\alpha(\mathbf{r})\rangle_{\rm id} \qquad (120)$$

for all $\alpha = 1, \ldots, M$,

For all $\alpha < M$, we may use the asymptotic equivalence of Ψ_α and Ω_α and the definition $\Phi_\alpha(\mathbf{r})/v = \langle C_\alpha(\mathbf{r})\rangle_{\rm id}$ to show that the RHS of Eq. (120) is asymptotically equivalent to the RHS of Eq. (20) for $D_\alpha = \delta H/\delta\Omega_\alpha$ in the incompressible theory.

For the remaining case $\alpha = M$, we may use Eq. (78) to show that that $\Psi_M = W_M + \zeta E_\alpha + Y_\alpha$, and use the definition $C_M(\mathbf{r}) = \mathbf{x}_M^T \mathbf{c}(\mathbf{r})$, to consider the limit

$$\lim_{\zeta\to\infty} \frac{\delta H}{\delta \Psi_\alpha(\mathbf{r})} = \lim_{\zeta\to\infty} \left\{ -\frac{M}{v\kappa_\alpha}[W_\alpha(\mathbf{r}) + \zeta E_M + Y_M(\mathbf{r})] + \mathbf{x}_M^T \langle \mathbf{c}(\mathbf{r})\rangle_{\rm id} \right\} \tag{121}$$

Using the limits $\mathbf{x}_M \to \mathbf{e}$, $\kappa_M \to \infty$, $E_M \to 1$, and $M\zeta/\kappa_\alpha \to 1$, along with the definition $c_0 = 1/v$, we obtain a limit

$$\lim_{\zeta\to\infty} \frac{\delta H}{\delta \Psi_\alpha(\mathbf{r})} = -c_0 + \mathbf{e}^T \langle \mathbf{c}(\mathbf{r})\rangle_{\rm id} \quad . \tag{122}$$

The RHS of Eq. (122) is equivalent to the RHS of Eq. (21) for $D_M(\mathbf{r})$ in the incompressible theory, thus demonstrating the asymtptotic equivalence of functional derivatives for $\alpha = M$, and thus for all $\alpha = 1, \ldots, M$.