Derivation and assessment of phase-shifted, disordered vector field models for frustrated solvent interactions

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The structure and properties of water at biological interfaces differ drastically from bulk due to effects including confinement and the presence of complicated charge distributions. This non-bulk-like behavior generally arises from water frustration, wherein all favorable interactions among water molecules cannot be simultaneously satisfied. While the frustration of interfacial water is ubiquitous in the cell, the role this frustration plays in mediating biophysical processes like protein folding is not well understood. To investigate the impact of frustration at interfaces, we here derive a general field theoretic model for the interaction of bulk and disordered vector fields at an embedded surface. We calculate thermodynamic and correlation functions for the model in two and three dimensions, and we compare our results to Monte Carlo simulations of lattice system analogs. In our analysis, we see that field-field cross correlations near the interface in the model give rise to a loss in entropy like that seen in glassy systems. We conclude by assessing our theory's utility as a coarse-grained model for water at polar biological interfaces. © 2013 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4792638>]

I. INTRODUCTION

The properties of water, both in the bulk phase and as a solvent, continue to elude a complete description that would demonstrate a full understanding of its physics. In the area of statistical physics, much effort has been put forth to explain the behavior of bulk water in its full phase space, with some success.¹ More recently, however, interest in water has spread to the area of biophysics, where the role water plays in mediating biomolecular processes is hotly debated. Seminal work on the hydrophobic effect, and the role water's hydrogen bond networks play in the attraction of non-polar bodies, has demonstrated the potential for water's unique properties to dominate physical behavior in biology.^{2,3}

The curious behavior of water in biophysical systems stems from the non-bulk-like water environments that biomolecular structures create. Whether next to membranes, inside protein cavities, or surrounding nucleic acids, water is subjected to conditions that forbid or frustrate its optimal hydrogen bond network and introduce new favorable interactions with its surroundings.

In many biological cases, water exists in a confined state that, depending on the degree of confinement and the topography of the confining container, demonstrates markedly different properties from bulk. Here, processes akin to the dewetting of solvent density between two plates can occur.⁴⁻⁸ Additionally, water at biomolecular interfaces exists in company with complex partial-charge distributions resulting from the diverse chemistry of amino acids, nucleic acids, and sugars. These charge distributions give rise to non-homogeneous

electric fields that can favor certain water dipole orientations in a spatially sensitive manner. As such, water will often be forced into a frustrated state in which all favorable interactions cannot be satisfied simultaneously.⁹⁻¹¹

When involved in processes like protein folding, water exists under both of the non-bulk-like conditions described here. Protein backbones and amino acid side chains generate complicated charged environments that impact nearby water molecules. Furthermore, proteins often fold in environments that confine surrounding water, as in complexes like protein chaperones and the ribosome exit tunnel.¹²⁻¹⁴ Even in the context of *in vitro* folding, water can become trapped in native or non-native pockets that can impact the kinetics and thermodynamics of the system. England and Pande have observed, among other effects, that frustration in a chaperonin cavity induces a slowing in water dynamics reminiscent of glassy behavior.¹² It is possible, thus, that unique water properties in these environments play a profound role in mediating the folding process.

Yet, in large scale simulations of protein folding, the role water plays in driving the dynamics is often neglected by necessity. In molecular dynamics (MD), the development of atomistic water models that accurately describe bulk behavior remains a challenge.¹⁵⁻¹⁸ The description of water in confined and charged environments places further demands on a model. Water models that include important properties like polarizability suffer from poor performance that limits their application to large scale simulations.¹⁹

Given the separation of timescales between water relaxation and protein conformational change, the explicit effects of water can be safely neglected in studying many slow processes. However, in cases like those mentioned above, water's role may be more pronounced. A simple understanding of how water behaves under frustrated conditions would go a

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long way in determining when, and to what extent, the role of water needs to be considered in protein folding models.

A litany of simple models for water give insight into its behavior under these non-bulk-like circumstances. Ising-like models have been used to describe confined, frustrated water on a lattice at the mean field level. Notably, England and Pande have used such models to show that water exhibits interesting behavior when confined between charged plates, and the two have compared their theoretical observations to large scale MD simulations.¹⁴ Two-dimensional vector models on a lattice have been used to investigate the impact of surface curvature on bulk and interfacial solvent configurations.²⁰ Two- and even three-dimensional water models like the Mercedes-Benz (MB) model have been able to accurately capture some bulk water properties. The characteristics of these models in confined or charged environments have been studied to some extent.^{21,22} Recent Landau-type field theories have been developed to describe water's behavior under confinement in supercooled phases.²³

Here, we aim to develop a model that sheds light on a general question: how does disorder localized at a particular surface impact solvent properties near that surface? Furthermore, how can the behavior resulting from frustration be characterized? To construct our model, we borrow elements from quantum field theory and solid-state physics to represent our system with continuum vector fields that interact at a disordering interface.^{24–33}

In developing this representation, we choose to include two separate vector fields in our model: a “bulk” vector field that interacts with itself over all space, and a random vector field that interacts with the bulk field only at an interface in the system. The values of the bulk field might represent something like the orientations of solvent molecules. Given the continuum formulation of the model, this field more realistically indicates an average orientation for a collection of molecules (e.g., an average collective dipole moment). The random vector field, on the other hand, will play the role of disorder in the model. Physically, the disordered field will represent something akin to the orientation of electric field lines or the presence of topographical features that one might find at a biological surface.

Given this coarse-grained representation of the system, do traditional vector field models (like the X-Y model) capture the effects of frustration?²⁷ If not, will similar models with different vector interaction angles describe such behavior more successfully? In this paper, we use thermodynamic and correlation functions, averaged over the random field, to analyze behavior near the model's disordered surface. We look in particular for the presence of frustration analogous to that seen in glassy systems. To complement our analytical theory, we will also perform lattice Monte Carlo calculations with a random field present on one side of the simulated system.³⁴

Below, we first describe the setup of our analytical theory. We go on to derive and analyze our model in two- and three-dimensional cases, and we compare our results to data collected through Monte Carlo simulations. We finish with a discussion of the biophysical implications that our results may possess.

II. THE MODEL

A. Analytical theory

We begin with a Hamiltonian density for our model expressed in terms of two n -component real vector fields $\vec{\psi}(\mathbf{x})$ and $\vec{\phi}(\mathbf{x})$ defined over the m -dimensional spatial coordinate $\mathbf{x}$:

$$\mathcal{H}\{\vec{\psi}(\mathbf{x}), \vec{\phi}(\mathbf{x})\} = \frac{1}{2} \langle \vec{\psi}(\mathbf{x}_1) | \Theta(\mathbf{x}_1, \mathbf{x}_2) | \vec{\psi}(\mathbf{x}_2) \rangle - \langle \vec{\psi}(\mathbf{x}) | \vec{\phi}(\mathbf{x}) \delta(\mathbf{x} \cdot \mathbf{x}_0) \rangle, \quad (1)$$

The brackets in the above expression represent a dot product between the enclosed vectors at the given spatial coordinate. As will be made clear below, the fields $\vec{\psi}(\mathbf{x})$ and $\vec{\phi}(\mathbf{x})$ have straightforward physical definitions: $\vec{\psi}(\mathbf{x})$ represents a bulk field with self-interaction, and $\vec{\phi}(\mathbf{x})$ represents a randomly distributed field that only interacts with $\vec{\psi}(\mathbf{x})$ on a plane. Throughout this paper, the dimensions will be restricted such that $n = m$.

The first term in this Hamiltonian density corresponds to the basic two-body self interaction for the field $\vec{\psi}(\mathbf{x})$, where the kernel $\Theta(\mathbf{x}_1, \mathbf{x}_2)$ is a generalized rotation matrix that modifies the geometry for low energy configurations of the field. For example, in the absence of any rotation kernel, $\vec{\psi}(\mathbf{x})$ vectors will relax to antiparallel two-body configurations. If $\Theta(\mathbf{x}_1, \mathbf{x}_2)$ is a $n \times n$ rotation matrix, the low energy (bulk) configurations will feature vectors skewed from the antiparallel by the given angle, introducing an effective phase shift in the model. Self-interaction is limited to the Gaussian level to maintain analytical tractability; the Gaussian approximation has also been shown to perform quite well in course-grained systems like the one formulated here due to the central limit theorem.^{27,32}

The second term in the Hamiltonian density accounts for the cross interaction between the $\vec{\psi}(\mathbf{x})$ and $\vec{\phi}(\mathbf{x})$ fields. The delta function is present to restrict the interaction to a plane: defining an arbitrary vector $\mathbf{x}_0$, the vectors normal to $\mathbf{x}_0$ define an $(m-1)$ -dimensional hyper-plane embedded in the m -dimensional space. Letting $\delta(\mathbf{x} \cdot \mathbf{x}_0)$ represent a standard Dirac measure, cross interactions contribute to the Hamiltonian only on this hyper-plane. Furthermore, in the interest of inducing disorder at the plane surface, $\vec{\phi}(\mathbf{x})$ will be a randomly distributed field (in magnitude and angle). The method for distributing and averaging over $\vec{\phi}(\mathbf{x})$ will be discussed below.

Computing our Hamiltonian by integrating over the coordinates $\mathbf{x}_1$ and $\mathbf{x}_2$, the partition function for our system can be expressed with the following functional integral:

$$Z = \int \mathcal{D}[\vec{\psi}] \exp \left(-\beta \int d\mathbf{x}_1 d\mathbf{x}_2 \mathcal{H}\{\vec{\psi}(\mathbf{x}), \vec{\phi}(\mathbf{x})\} \right). \quad (2)$$

After introducing an auxiliary field and completing the square, this partition function can be evaluated to yield a closed functional form:^{32,33}

$$Z = \frac{1}{\beta^{n/2} \sqrt{\det \Theta(\mathbf{x}_1, \mathbf{x}_2)}} \exp \left(\frac{\beta}{4} \int d\mathbf{x}_1 d\mathbf{x}_2 \langle \vec{\phi}(\mathbf{x}_1) \delta(\mathbf{x}_1 \cdot \mathbf{x}_0) | \Theta^{-1}(\mathbf{x}_1, \mathbf{x}_2) | \vec{\phi}(\mathbf{x}_2) \delta(\mathbf{x}_2 \cdot \mathbf{x}_0) \rangle \right). \quad (3)$$

Here, we have already made an assumption of translational invariance, the full ramifications of which will be discussed later. Formally, this assumption restricts our results to the area at and along our embedded surface.

To proceed with our derivation, we now need to discuss the properties of our designated “random” field $\vec{\phi}(\mathbf{x})$. As a physical analogy, we wish $\vec{\phi}(\mathbf{x})$ to play the role of something like a biomolecular interface, describing a random charge or topographical distribution confined to the system’s embedded plane. The vectors of $\vec{\psi}(\mathbf{x})$ will interact with the random $\vec{\phi}(\mathbf{x})$ only near the embedded plane, so that frustration (the inability to satisfy both ϕ/ψ interactions and ψ/ψ interactions simultaneously) may then ensue at the surface. In the context of biomolecules, we will allow this random field to be dynamic: if hypothetical moieties and charges are imbedded in a liquid membrane or coupled to side-chain motions in a protein, their corresponding field should be able to fluctuate over time. Accordingly, we would like $\vec{\phi}(\mathbf{x})$ to be able to change at equilibrium, i.e., be an annealed quantity.

To calculate the thermodynamic functions and correlation functions of interest, we need to base our theory on the annealed-average partition function for the system, Z_{ann} . For simplicity, we define the (unnormalized) probability distribution over $\vec{\phi}(\mathbf{x})$ to be Gaussian with zero mean and standard deviation σ :^{25,26,29}

$$\mathcal{P}\{\vec{\phi}(\mathbf{x})\} = \exp\left(-\frac{1}{2\sigma^2} \int d\mathbf{x} \langle \vec{\phi}(\mathbf{x}) | \vec{\phi}(\mathbf{x}) \rangle\right). \quad (4)$$

Based on this probability distribution, the annealed-average partition function is given by the following expression:

$$Z_{ann} = \int \mathcal{D}[\vec{\phi}] \mathcal{P}\{\vec{\phi}(\mathbf{x})\} Z\{\vec{\phi}(\mathbf{x})\}. \quad (5)$$

To evaluate this integral in closed-form fashion, we merely need to merge the two integral kernels from $\mathcal{P}\{\vec{\phi}(\mathbf{x})\}$ and $Z\{\vec{\phi}(\mathbf{x})\}$. We will call this merged kernel $\Gamma(\mathbf{x}_1, \mathbf{x}_2)$:

$$\begin{aligned} \Gamma(\mathbf{x}_1, \mathbf{x}_2) &= (\delta(\mathbf{x}_1 - \mathbf{x}_2) \mathbf{I} - \frac{1}{2} \sigma^2 \beta \Theta^{-1}(\mathbf{x}_1, \mathbf{x}_2)) \delta(\mathbf{x}_1 \cdot \mathbf{x}_0) \\ &\quad \times \delta(\mathbf{x}_2 \cdot \mathbf{x}_0), \end{aligned} \quad (6)$$

where $\mathbf{I}$ is the identity matrix in the n -dimensional rotational space. Plugging in this relation for the kernel, the expression for the annealed-average partition function is now given by

$$\begin{aligned} Z_{ann} &= \frac{1}{\beta^{n/2} \sqrt{\det \Theta(\mathbf{x}_1, \mathbf{x}_2)}} \times \int \mathcal{D}[\vec{\phi}] \\ &\quad \times \exp\left(-\frac{1}{2\sigma^2} \int d\mathbf{x}_1 d\mathbf{x}_2 \langle \vec{\phi}(\mathbf{x}_1) | \Gamma(\mathbf{x}_1, \mathbf{x}_2) | \vec{\phi}(\mathbf{x}_2) \rangle\right). \end{aligned} \quad (7)$$

This integral can be evaluated directly by Gaussian functional integration, leading to the final expression for Z_{ann} :

$$Z_{ann} = \frac{1}{\beta^{n/2} \sqrt{\det \Theta(\mathbf{x}_1, \mathbf{x}_2)}} \times \frac{1}{\sqrt{\det \Gamma(\mathbf{x}_1, \mathbf{x}_2)}}. \quad (8)$$

We should note that this result is contingent on the invertibility of $\Gamma(\mathbf{x}_1, \mathbf{x}_2)$, as will become evident in calculating correlation functions for the theory. Upon quick inspection of

the kernel $\Gamma(\mathbf{x}_1, \mathbf{x}_2)$, we see that the free theory is recovered when $\sigma \rightarrow 0$ (i.e., when the field goes to zero), as one should require.

To calculate the observables of our theory, we need to introduce functional and matrix forms for the kernels $\Theta(\mathbf{x}_1, \mathbf{x}_2)$ and $\Gamma(\mathbf{x}_1, \mathbf{x}_2)$. These expressions will be introduced below in Sec. III.

III. RESULTS AND DISCUSSION

As a preface to continuing our theoretical derivation, we note that our systems differ from those commonly studied in three major ways: (1) we study systems under annealed disorder (disorder that can change on a timescale of system relaxation), (2) we restrict disorder to an interface in the system, and (3) we introduce phase shifts into the Hamiltonian that alter the optimal vector-pair interaction. Since our disorder is annealed, we do not expect to observe true spin glass behavior in our model; rather, we expect to see frustration that would change in microscopic character over time. The thermodynamic and correlation properties that result from this disorder are derived below.

A. Analytical theory – The X-Y regime

1. The partition function

Before we proceed with our derivation, we need to choose a dimensionality in which to place our vector fields. In this paper, we will focus most of our theory on the ($m = 2$, $n = 2$)-dimensional regime occupied by the X-Y model. The physics of the true X-Y model (in the absence of phase shifts) is well explored: in particular due to its applications to solid state physics, the X-Y model has been thoroughly studied with Monte Carlo simulations and analytical theory, both with well ordered and disordered interactions.^{24–31,34–36} Restriction to two dimensions greatly simplifies the algebra of our theory, which later allows for full comparison of our model’s predictions to Monte Carlo data.

We should note, however, that two-dimensional systems bring some additional difficulty to the problem. The X-Y model exists at the lower critical dimension for order that persists in the presence of fluctuations, and complications in interpreting thermodynamic properties result. In general, it is well accepted that the bulk X-Y model exhibits a “quasi-ordered” low temperature phase that is broken by topological deformations. The addition of disorder further muddles the description of phase behavior, where the existence of spin glass or reentrant phase transitions can be supported or disputed by various analytical techniques. X-Y-type spin glasses under quenched disorder, both with non-random and uniform random interactions, remain a subject of controversy in statistical physics.^{24–26,29–31,34–36}

Given the natural interest in three-dimensional systems, we also present theory and Monte Carlo data for the ($m = 3$, $n = 3$)-dimensional regime of the so-called Heisenberg model. Unlike the X-Y model, the Heisenberg model (in the absence of phase shifts) exhibits a well ordered low-temperature phase.^{31,32} Quenched disorder spin glass systems

in the Heisenberg regime have also been investigated.^{37,38} We will later discuss the tractable extensions of our theory to three dimensions, but we do not here derive the general phase-shifted model in the Heisenberg regime. Nonetheless, we compare what observables we can predict analytically with those calculated from three-dimensional Monte Carlo simulations.

Restricting ourselves to the ($m = 2, n = 2$)-dimensional regime, we will first compute the observables of our analytical theory. To define expressions for our kernels, we set the angular part of $\Theta(\mathbf{x}_1, \mathbf{x}_2)$ to be a simple 2×2 rotation matrix with angle θ . We also need to include a specific spatial dependence for Θ , which we choose so that interactions occur at the nearest-neighbor level. Introducing an arbitrarily small lattice spacing a , the full form of $\Theta(\mathbf{x}_1, \mathbf{x}_2)$ is given by

$$\Theta(\mathbf{x}_1, \mathbf{x}_2) = \begin{pmatrix} \cos \theta & -\sin \theta \\ \sin \theta & \cos \theta \end{pmatrix} [\delta(\mathbf{x}_1 - \mathbf{x}_2 - a) + \delta(\mathbf{x}_1 - \mathbf{x}_2 + a)].$$

The definition of $\Gamma(\mathbf{x}_1, \mathbf{x}_2)$ in the X-Y regime follows trivially from the above definition of $\Theta(\mathbf{x}_1, \mathbf{x}_2)$ and Eq. (6). Now, to compute an explicit expression for our partition function, we need to calculate the determinants of our two kernels based on Eq. (8). Since $\Theta(\mathbf{x}_1, \mathbf{x}_2)$ is an orthogonal transformation, it has a trivial unit determinant. The expression of interest has now reduced to

$$Z_{ann} = \frac{1}{\beta \sqrt{\det \Gamma(\mathbf{x}_1, \mathbf{x}_2)}}. \quad (9)$$

The determinant of $\Gamma(\mathbf{x}_1, \mathbf{x}_2)$, however, is not trivial to calculate, especially given the presence of two planar delta functions in Eq. (6). To simplify our calculation, we split Γ into trivial and “interacting” portions: $\Gamma = \Gamma_0 + \Gamma_I$, where

$$\Gamma_0 = \delta(\mathbf{x}_1 - \mathbf{x}_2) \mathbf{I} \times \delta(\mathbf{x}_1 \cdot \mathbf{x}_0) \delta(\mathbf{x}_2 \cdot \mathbf{x}_0) \quad (10)$$

and

$$\Gamma_I = -\frac{1}{2} \sigma^2 \beta \Theta^{-1}(\mathbf{x}_1, \mathbf{x}_2) \delta(\mathbf{x}_1 \cdot \mathbf{x}_0) \delta(\mathbf{x}_2 \cdot \mathbf{x}_0). \quad (11)$$

Since we can diagonalize the matrix Γ_0 exactly, we treat Γ_I as a perturbation (expanded in small $\sigma^2 \beta$) and calculate its eigenvalues to first order. The product of these eigenvalues then yields the desired determinant at a first order approximation. Introducing a placeholder variable k and invoking the properties of the delta measure $\delta(\mathbf{x}_2 \cdot \mathbf{x}_0)$, we solve the zeroth-order eigenvalue equation easily,

$$\begin{aligned} \int d\mathbf{x}_2 \delta(\mathbf{x}_1 - \mathbf{x}_2) \delta(\mathbf{x}_1 \cdot \mathbf{x}_0) \delta(\mathbf{x}_2 \cdot \mathbf{x}_0) \xi(\mathbf{x}_1) &= \lambda \xi(\mathbf{x}_1) \\ \int d\mathbf{x}_2 \delta(\mathbf{x}_1 - \mathbf{x}_2) \delta(\mathbf{x}_1 \cdot \mathbf{x}_0) \delta(\mathbf{x}_2 \cdot \mathbf{x}_0) \delta(\mathbf{x}_1 - \mathbf{k}) \delta(\mathbf{x}_1 \cdot \mathbf{x}_0) \\ &= \delta(\mathbf{x}_1 - \mathbf{k}) \delta(\mathbf{x}_1 \cdot \mathbf{x}_0), \end{aligned}$$

which implies Γ_0 has the eigenfunctions $\xi(\mathbf{x}_1) = \delta(\mathbf{x}_1 - \mathbf{k}) \delta(\mathbf{x}_1 \cdot \mathbf{x}_0)$, $\forall \mathbf{k} \in \mathbb{R}^3$, with an infinite space of degenerate (unit) eigenvalues. We note that, with the presence of the identity matrix in Eq. (10), the eigenvalues of Γ_0 in the two-dimensional rotational space are also unit and degenerate. The

zeroth-order eigenvectors in the rotational space are simply the columns of the identity matrix.

With our zeroth-order solutions in hand, we can compute the eigenvalue corrections by evaluating the following matrix element:

$$\langle \xi(\mathbf{x}_1) | -\frac{1}{2} \sigma^2 \beta \Theta^{-1}(\mathbf{x}_1, \mathbf{x}_2) \delta(\mathbf{x}_1 \cdot \mathbf{x}_0) \delta(\mathbf{x}_2 \cdot \mathbf{x}_0) | \xi(\mathbf{x}_2) \rangle. \quad (12)$$

In translational space, this expression can be evaluated with little effort. Introducing placeholder variables $\mathbf{j}$ and $\mathbf{k}$, we have

$$\begin{aligned} \langle \xi(\mathbf{x}_1) | \Gamma_I | \xi(\mathbf{x}_2) \rangle &= \int d\mathbf{x}_1 d\mathbf{x}_2 \xi(\mathbf{x}_1) \Gamma_I \xi(\mathbf{x}_2) \\ &= - \int d\mathbf{x}_1 d\mathbf{x}_2 \delta(\mathbf{x}_1 - \mathbf{j}) \delta(\mathbf{x}_1 \cdot \mathbf{x}_0) \\ &\quad \times \frac{1}{2} \sigma^2 \beta \Theta^{-1}(\mathbf{x}_1, \mathbf{x}_2) \delta(\mathbf{x}_2 - \mathbf{k}) \delta(\mathbf{x}_2 \cdot \mathbf{x}_0). \end{aligned}$$

These delta functions act as collective sifting functions for the variables $\mathbf{j}$ and $\mathbf{k}$, and we derive the result

$$\langle \xi(\mathbf{x}_1) | \Gamma_I | \xi(\mathbf{x}_2) \rangle = -\frac{1}{2} \sigma^2 \beta \Theta^{-1}(\mathbf{j}, \mathbf{k}) \delta(\mathbf{j} \cdot \mathbf{x}_0) \delta(\mathbf{k} \cdot \mathbf{x}_0), \quad (13)$$

which we note is non-zero only when $\mathbf{j} \cdot \mathbf{x}_0 = 0$ and $\mathbf{k} \cdot \mathbf{x}_0 = 0$.

Fixing $\mathbf{j}$ and $\mathbf{k}$ such that Eq. (13) is non-zero, we will now calculate the eigenvalue corrections in rotational space. Before we go on to the calculation, we need to discuss one minor caveat: we expect the perturbation to break the degeneracy of the zeroth-order rotational eigenvalues, as $\Theta^{-1}(\mathbf{x}_1, \mathbf{x}_2)$ introduces complicated rotational behavior into our model. Accordingly, our eigenvalue corrections will not be invariant to our choice of basis, and we need to use degenerate perturbation theory. To do so, we need to solve the following matrix equation (in which $\Gamma_I = -\frac{1}{2} \sigma^2 \beta \Theta^{-1}(\mathbf{j}, \mathbf{k})$):

$$\begin{vmatrix} \langle \mathbf{e}_1 | \Gamma_I | \mathbf{e}_1 \rangle - \lambda' & \langle \mathbf{e}_1 | \Gamma_I | \mathbf{e}_2 \rangle \\ \langle \mathbf{e}_2 | \Gamma_I | \mathbf{e}_1 \rangle & \langle \mathbf{e}_2 | \Gamma_I | \mathbf{e}_2 \rangle - \lambda' \end{vmatrix} = 0,$$

where $\mathbf{e}_1$ and $\mathbf{e}_2$ are the first and second eigenvectors of the identity matrix, respectively.³⁹ This equation has the solutions $\lambda' = -\frac{1}{2} \sigma^2 \beta \cos \theta \pm i \frac{1}{2} \sigma^2 \beta \sin \theta$, meaning our corrected eigenvalues are given by

$$\lambda_{corr} = 1 - \frac{1}{2} \sigma^2 \beta \cos \theta \pm i \frac{1}{2} \sigma^2 \beta \sin \theta. \quad (14)$$

As the zeroth-order rotational space has two fully degenerate eigenvalues, there is no approximation to the corrected eigenvalues above first order.

Since $\det \Gamma$ to first order is simply a product of these corrected eigenvalues, we finally have a closed form expression for the annealed-average partition function Z_{ann} :

$$Z_{ann} = \frac{1}{\beta \sqrt{1 - \sigma^2 \beta \cos \theta + \frac{1}{4} \sigma^4 \beta^2}}. \quad (15)$$

Before we go on to calculate the observables of this partition function, we should briefly review the approximations made in this theory thus far. Prior to introducing a functional form for our rotation matrix, the theory is essentially exact. However, the Gaussian approximation in $\vec{\psi}$ is implicit in our

model, and we assume that interactions at ψ^4 are averaged-over and thus ineffectual. While this approximation should perform well at standard temperatures, we expect our model to break down at low temperatures, where configurational diversity will drop due to the absence of higher terms in $\bar{\psi}$.

Additionally, when we perturbatively solved for the determinant of Γ , we expanded the interacting portion of our kernel in the parameter $\sigma^2\beta$. Accordingly, we can expect our theory to be valid for relatively “small” values of this expansion parameter. Saying, without loss of generality, that our theory will apply for values of $\sigma^2\beta$ less than some constant b of order one, simple algebraic manipulation indicates our expected regime of validity:

$$\beta\sigma^2 < b$$

$$kT > \frac{\sigma^2}{b}.$$

Thus, we expect our model to be valid for temperatures above a constant set by the square of the disorder’s standard deviation.

With respect to spatial dependence, all interactions in the model are restricted to be nearest-neighbor in nature. We have also fixed the vectors $\mathbf{j}$ and $\mathbf{k}$ such that our eigenvalue corrections are non-zero. Based on the presence of the planar delta functions in $\mathbf{j}$ and $\mathbf{k}$, the thermodynamic observables of this partition function will thus only describe field-field interactions near the embedded plane (after the introduction of a lattice spacing a). These functions, of course, are the important observables for this model, since we are interested in phase behavior near the surface-bulk interface. As we will mention further, it is possible that two-point correlation functions calculated with this translational invariance requirement describe some additional properties of the bulk system.

2. Thermodynamic functions

With a simple expression for the partition function now in hand, we can calculate thermodynamic functions of the model that will provide insight into phase behavior. As a first step, we calculate the annealed-average free energy of the model, F_{ann} , given by the formula

$$F_{ann} = -\frac{1}{\beta} \ln Z_{ann}$$

$$= -\frac{1}{\beta} \ln \left(\frac{1}{\beta \sqrt{1 - \sigma^2\beta \cos \theta + \frac{1}{4}\sigma^4\beta^2}} \right). \quad (16)$$

To further aid in our analysis, we can calculate the annealed-average entropy S_{ann} based on this free energy

$$S_{ann} = -\frac{\partial F_{ann}}{\partial T}. \quad (17)$$

The constant volume heat capacity, $C_{v,ann}$, is also given by its standard formula

$$C_{v,ann} = T \frac{\partial S_{ann}}{\partial T}. \quad (18)$$

Figures 1–3 show the free energy, entropy, and heat capacity plotted versus T at various model angles θ and a fixed

FIG. 1. Free energy versus T at constant $\sigma = 0.75$ for various model angles θ . Temperature is reported in natural units such that $k = 1$.

$\sigma = 0.75$. Temperature units have been chosen naturally so that $k = 1$ in all cases. A number of features in these plots are notable, and we discuss these properties in depth below.

First, we see that all three thermodynamic properties diverge in the neighborhood of $kT = 0.3$ when the model angle θ is set to zero. Indeed, Eq. (15) indicates that the annealed averaged partition function exhibits an analytical divergence at $\theta = 0$. While this divergence is non-physical, it suggests the emergence of a stable phase near $T = 0.3$. When $\theta > 0$, the

FIG. 2. Entropy versus T at constant $\sigma = 0.75$ for various model angles θ . Temperature is reported in natural units such that $k = 1$. The line at $T = 0$ represents the entropy freezing transition threshold for the models.

FIG. 3. Constant volume heat capacity versus T at constant $\sigma = 0.75$ for various model angles θ . Energy is reported in natural units such that $k = 1$.

analytical divergence in the model disappears, but free energy minima persist until a critical point in θ - T space at $\theta \approx \pi/8$.

More interesting, however, are the free energy maxima that can be seen in Figure 1 at slightly higher temperatures. The clearest characterization of these features can be derived from Figure 2: in three cases, the entropy goes to zero (i.e., the model “freezes” to an effective single configuration) at a temperature greater than zero. This behavior would normally suggest that, near the surface, the model becomes “frustrated” by the disordered field and enters a glass-like phase with significantly reduced entropy.

We need to mention, however, that our model freezes even in the $\sigma = 0$ case: the Gaussian approximation in the $\bar{\psi}$ field should and does cause a considerable loss in entropy in that field. The $\sigma = 0$ free energy, from Eq. (16), is given by $F = -kT \log(kT)$. Accordingly, the $\sigma = 0$ model entropy goes to zero at $T = 1/e$ in natural units. Any generic freezing that occurs at or below this temperature needs to be regarded as an artifact of approximations made to the model. It is likely that all results below this threshold temperature should be interpreted as being non-physical.

However, we see that the entropy goes to zero above this threshold temperature $T = 1/e$ over a significant volume of parameter space. We conclude, in these cases, that the model undergoes a transition into a frustrated, low-entropy phase that is induced by the random field. Certainly, the nature of entropy curves below the freezing transition needs to be considered non-physical; between the freezing temperature and the Gaussian threshold temperature, the true entropy of the frustrated system should remain around zero. As indicated by Figure 2, models at both small ($\theta \approx 0$) and large ($\theta = \pi$) phase shifts undergo a freezing transition into a ϕ -induced phase.

At smaller values of θ an entropy minimum arises with the introduction of non-zero σ . For models in this small θ range, the emergence of this minimum is responsible for in-

FIG. 4. Entropy at various values of σ for the $\theta = \pi/12$ model. The entropy minimum induced by the presence of non-zero σ induces a higher temperature freezing transition than appears in the $\sigma = 0$ case for three of the four models shown in the plot.

ducing the low-entropy freezing transition. No such entropy minimum occurs in models that freeze at $\theta \approx \pi$. Figure 4 shows the entropy as a function of temperature for the $\theta = \pi/12$ model at various values of σ . The entropy minimum gives rise to field-induced freezing transitions at $\sigma = 0.4$, $\sigma = 0.6$, and $\sigma = 0.8$. Figure 3 illustrates that the transition into the entropy minimum in Figure 2 corresponds to an (albeit small) maximum in the heat capacity that disappears with increasing θ .

As σ increases, entropy minima become more pronounced and models at a wider range of θ undergo the freezing transition. In Figure 4, the freezing transition disappears at $\sigma = 1$; however, a deep entropy minimum remains, suggesting that the disorder still induces a significant drop in configurational diversity. We should also note that, as σ increases to 1, our model nears our predicted regime of invalidity where $kT \leq \sigma^2$.

These observations imply that, for some values of θ and σ , a $\bar{\phi}$ -induced frozen phase is present in our theory. This phase arises from an instability in the model: an unfavorable entropy decrease at large σ becomes more pronounced until the configuration freezes at $S = 0$. Entropy minima that do not reach zero are present in a large region of parameter space, suggesting that disorder-induced frustration and a resultant loss of configurational diversity is widespread. This behavior is indeed reminiscent of thermodynamic glasses, where frustration due to random interactions slows equilibrium dynamics.

Figures 5–7 illustrate aspects of the phase diagram for this $\bar{\phi}$ -induced frozen phase. Figure 5 shows the constant $\theta = \pi/12$ projection of the diagram in the σ - T plane, where the $\sigma = 0$ line is drawn in for reference. Figure 6 plots a constant $\sigma = 0.75$ projection in the θ - T plane, where the Gaussian freezing line is again drawn for reference. A critical point exists at $\theta \approx \pi/9$, beyond which models with higher values of

FIG. 5. Phase diagram projection in σ -temperature space for fixed model $\theta = \pi/12$. The horizontal line indicates the entropy deficit seen in the $\sigma = 0$ case. The phase line shown reaches the $\sigma = 0$ limit at approximately $\sigma = 0.1$.

θ do not freeze. The σ -induced phase reemerges at values of θ beyond about $2\pi/3$. Finally, Figure 7 shows the full phase diagram for the system as a function of θ and σ , where the shaded plane indicates the $\sigma = 0$ freezing energy.

The area of parameter space in which disorder induces an entropy minimum, but not a true freezing transition, extends just past the $\theta = \pi/4$ plane of the full phase diagram. While these entropy minima do not correspond to a true thermodynamic phase, they still indicate a loss of configurations induced by the presence of disorder.

3. Cross-correlation function

While the above thermodynamic quantities describe the interesting macroscopic properties of our system, behavior at the microscopic and mesoscopic levels is also fundamentally intriguing. Field-field correlation functions, along with

FIG. 6. Phase diagram projection in θ -temperature space with fixed $\sigma = 0.75$. Again, the horizontal line indicates the entropy lost in the $\sigma = 0$ model. A lower critical point in temperature exists at approximately $\theta = \pi/9$ for this value of σ ; a σ -induced frozen phase reemerges at around $\theta = 2\pi/3$.

FIG. 7. Full phase diagram for $\vec{\phi}$ - $\vec{\psi}$ system over parameters T , σ , and θ . The dark horizontal plane located at $T = 1/e$ indicates the entropy deficit to the Gaussian approximation at $\sigma = 0$. Thus, areas below the protruding surfaces but above the horizontal plane represent a σ -induced phase in the model. The critical line (made up of critical points like that seen in Figure 10) can be seen on the edge of the surface at relatively small θ .

their associated correlation lengths, provide an avenue to extract such behavior. As in our investigation of thermodynamic properties, our primary goal with correlation functions is to study the phenomena that are induced by the introduction of the random field $\vec{\phi}$. Accordingly, the connected $\vec{\phi} - \vec{\psi}$ cross-correlation function, $\langle \vec{\phi}(\mathbf{x}_1), \vec{\psi}(\mathbf{x}_2) \rangle$, will provide the most information regarding the impact of $\vec{\phi}$ on the bulk field $\vec{\psi}$.

In order to calculate $\langle \vec{\phi}(\mathbf{x}_1), \vec{\psi}(\mathbf{x}_2) \rangle$, we first introduce two “source” vector fields, $\vec{J}(\mathbf{x})$ and $\vec{J}'(\mathbf{x})$, into the model Hamiltonian density:

$$\begin{aligned} \mathcal{H}\{\vec{\psi}(\mathbf{x}), \vec{\phi}(\mathbf{x})\} = & \langle \vec{\psi}(\mathbf{x}_1) | \Theta(\mathbf{x}_1, \mathbf{x}_2) | \vec{\psi}(\mathbf{x}_2) \rangle \\ & + \langle \vec{\psi}(\mathbf{x}) | \vec{\phi}(\mathbf{x}) \delta(\mathbf{x} \cdot \mathbf{x}_0) \rangle \\ & + \langle \vec{\phi}(\mathbf{x}) | \vec{J}(\mathbf{x}) \rangle + \langle \vec{\psi}(\mathbf{x}) | \vec{J}'(\mathbf{x}) \rangle. \end{aligned}$$

We can now use the common source derivative method to calculate the correlation function $\langle \vec{\phi}(\mathbf{x}_1), \vec{\psi}(\mathbf{x}_2) \rangle$:

$$\langle \vec{\phi}(\mathbf{x}_1), \vec{\psi}(\mathbf{x}_2) \rangle = \frac{\partial^2 \log Z_{\text{ann}}(\vec{J}(\mathbf{x}), \vec{J}'(\mathbf{x}))}{\partial \vec{J}(\mathbf{x}_1) \partial \vec{J}'(\mathbf{x}_2)} \Big|_{\vec{J}, \vec{J}' \rightarrow 0}, \quad (19)$$

where, since $\vec{J}(\mathbf{x})$ and $\vec{J}'(\mathbf{x})$ are vector sources, each derivative term represents an n -component gradient operator.^{32,33} Prior to performing these derivatives, however, we must first calculate $Z_{\text{ann}}(\vec{J}(\mathbf{x}), \vec{J}'(\mathbf{x}))$. In the interest of maintaining notational simplicity, we record only the resultant Hamiltonian density (i.e., the exponent of the functional integral being performed) during the integration process.

In analogy to Eq. (3), we compute the integral over $\vec{\psi}$ by simply completing the square in $\vec{\psi}$. The resultant Hamiltonian

density is given by

$$\begin{aligned}\mathcal{H}'\{\vec{\psi}(\mathbf{x}), \vec{\phi}(\mathbf{x})\} = & \langle \vec{\phi}(\mathbf{x}_1) | \Theta^{-1}(\mathbf{x}_1, \mathbf{x}_2) | \vec{\phi}(\mathbf{x}_2) \rangle \\ & + \langle \vec{\phi}(\mathbf{x}_1) | \Theta^{-1}(\mathbf{x}_1, \mathbf{x}_2) | \vec{J}'(\mathbf{x}_2) \rangle \\ & + \langle \vec{J}'(\mathbf{x}_1) | \Theta^{-1}(\mathbf{x}_1, \mathbf{x}_2) | \vec{\phi}(\mathbf{x}_2) \rangle \\ & + \langle \vec{J}'(\mathbf{x}_1) | \Theta^{-1}(\mathbf{x}_1, \mathbf{x}_2) | \vec{J}'(\mathbf{x}_2) \rangle \\ & + \langle \vec{\phi}(\mathbf{x}) | \vec{J}(\mathbf{x}) \rangle.\end{aligned}$$

Based on the derivatives we plan to take, we can simplify this expression by eliminating terms that contain $\vec{J}'(\mathbf{x}_1)$:

$$\mathcal{H}'\{\vec{\psi}(\mathbf{x}), \vec{\phi}(\mathbf{x})\} = \langle \vec{\phi}(\mathbf{x}_1) | \Theta^{-1}(\mathbf{x}_1, \mathbf{x}_2) | \vec{\phi}(\mathbf{x}_2) \rangle + \langle \vec{\phi}(\mathbf{x}_1) | \Theta^{-1}(\mathbf{x}_1, \mathbf{x}_2) | \vec{J}'(\mathbf{x}_2) \rangle + \langle \vec{\phi}(\mathbf{x}) | \vec{J}(\mathbf{x}) \rangle.$$

Now, to perform the integral over $\vec{\phi}$, we complete the square with respect to $\vec{\phi}$ to yield

$$\begin{aligned}\mathcal{H}''\{\vec{\psi}(\mathbf{x}), \vec{\phi}(\mathbf{x})\} = & \langle \Theta^{-1}(\mathbf{x}_1, \mathbf{x}_2) \vec{J}'(\mathbf{x}_1) | \Gamma^{-1}(\mathbf{x}_1, \mathbf{x}_2) | \Theta^{-1}(\mathbf{x}_1, \mathbf{x}_2) \vec{J}'(\mathbf{x}_2) \rangle \\ & + \langle \Theta^{-1}(\mathbf{x}_1, \mathbf{x}_2) \vec{J}'(\mathbf{x}_1) | \Gamma^{-1}(\mathbf{x}_1, \mathbf{x}_2) | \vec{J}(\mathbf{x}_2) \rangle \\ & + \langle \vec{J}(\mathbf{x}_1) | \Gamma^{-1}(\mathbf{x}_1, \mathbf{x}_2) | \Theta^{-1}(\mathbf{x}_1, \mathbf{x}_2) \vec{J}'(\mathbf{x}_2) \rangle \\ & + \langle \vec{J}(\mathbf{x}_1) | \Gamma^{-1}(\mathbf{x}_1, \mathbf{x}_2) | \vec{J}(\mathbf{x}_2) \rangle,\end{aligned}$$

and finally, eliminating terms that do not contain both $\vec{J}(\mathbf{x}_1)$ and $\vec{J}'(\mathbf{x}_2)$, we are left with

$$\mathcal{H}''\{\vec{\psi}(\mathbf{x}), \vec{\phi}(\mathbf{x})\} = \langle \vec{J}(\mathbf{x}_1) | \Gamma^{-1}(\mathbf{x}_1, \mathbf{x}_2) | \Theta^{-1}(\mathbf{x}_1, \mathbf{x}_2) \vec{J}'(\mathbf{x}_2) \rangle.$$

Recognizing $\mathcal{H}''(\mathbf{x}_1, \mathbf{x}_2)$ as the exponential argument in Z_{ann} , we perform our derivatives and set the source terms to zero to find

$$\begin{aligned}\langle \vec{\phi}(\mathbf{x}_1), \vec{\psi}(\mathbf{x}_2) \rangle = & \frac{\partial^2 \log Z_{ann}(\vec{J}(\mathbf{x}), \vec{J}'(\mathbf{x}))}{\partial \vec{J}(\mathbf{x}_1) \partial \vec{J}'(\mathbf{x}_2)} \Big|_{J, J' \rightarrow 0} \\ = & \langle \vec{o}(\mathbf{x}_1) | \Gamma^{-1}(\mathbf{x}_1, \mathbf{x}_2) | \Theta^{-1}(\mathbf{x}_1, \mathbf{x}_2) \vec{o}(\mathbf{x}_2) \rangle,\end{aligned}\quad (20)$$

where $\vec{o}(\mathbf{x})$ is an n -dimensional constant vector containing all unit entries. Equation (20) represents the general expression for the cross-correlation function $\langle \vec{\phi}(\mathbf{x}_1), \vec{\psi}(\mathbf{x}_2) \rangle$ in our model.

To calculate the correlation function in the X-Y regime, we need to insert our specific expressions for $\Theta(\mathbf{x}_1, \mathbf{x}_2)$ and $\Gamma(\mathbf{x}_1, \mathbf{x}_2)$ as given earlier and invert the two kernels over the full coordinate space. To do so, we choose to make two simplifying approximations. First, to facilitate Fourier transformation, we invoke full translational invariance in $\Gamma(\mathbf{x}_1, \mathbf{x}_2)$ by forcing the two planar δ -functions to be non-zero. Second, we make a “low momentum” approximation in Fourier- $\mathbf{q}$ space by setting $\cos \mathbf{q} \approx 1 - \mathbf{q}^2$. The necessity and ramifications of these approximations will be discussed later. We now proceed to invert $\Theta(\mathbf{x}_1, \mathbf{x}_2)$ and $\Gamma(\mathbf{x}_1, \mathbf{x}_2)$ in Fourier and rotational space.

Starting with the component $\Theta_{ij}(\mathbf{x}_1, \mathbf{x}_2) = \Theta_{ij\theta}[\delta(\mathbf{x}_1 - \mathbf{x}_2 - a) + \delta(\mathbf{x}_1 - \mathbf{x}_2 + a)]$, we Fourier transform using the conjugate variable $\mathbf{x}_1 - \mathbf{x}_2$ to find

$$\begin{aligned}\Theta_{ij}(\mathbf{q}) = & \Theta_{ij\theta} \cos a\mathbf{q} \\ \approx & \Theta_{ij\theta} (1 - a\mathbf{q}^2),\end{aligned}\quad (21)$$

where a is an arbitrary lattice spacing. In this case, our Fourier components and rotation space are independent, and we can factor the momentum-dependent terms from the rotation matrix. We invert $\Theta_{ij}(\mathbf{q})$ in two steps, first with matrix inversion for $\Theta_{ij\theta}$ and then a simple multiplicative inversion on the Fourier components, yielding

$$\Theta_{ij}^{-1}(\mathbf{q}) \approx \Theta_{ij\theta}^{-1} (1 + a\mathbf{q}^2), \quad (22)$$

where we have used the further approximation $1/(1 - a\mathbf{q}^2) \approx (1 + a\mathbf{q}^2)$ for small $\mathbf{q}$.

To invert the components of $\Gamma(\mathbf{x}_1, \mathbf{x}_2)$ we make one last simplifying approximation: we assume that terms off the diagonal of Γ do not contribute significantly to the correlation function, and set $\Gamma_{12} = \Gamma_{21} = 0$. Under this approximation, Γ is diagonal both in Fourier space and the rotational space, and we compute its inverse simply by inverting its components

$$\Gamma_{11}^{-1}(\mathbf{q}) = \Gamma_{22}^{-1}(\mathbf{q}) \approx \frac{1}{\det \Gamma (1 - (1 + a\mathbf{q}^2) \Theta_{11\theta} \sigma^2 \beta / 2)}.$$

(23)

Given these expressions for the inverse kernels, we can express our correlation function in Fourier space as

$$\begin{aligned}\langle \vec{\phi}(\mathbf{x}_1), \vec{\psi}(\mathbf{x}_2) \rangle_{\mathbf{q}} = & \Gamma_{11}^{-1}(\mathbf{q}) (\Theta_{11}^{-1}(\mathbf{q}) + \Theta_{12}^{-1}(\mathbf{q})) \\ & + \Gamma_{22}^{-1}(\mathbf{q}) (\Theta_{21}^{-1}(\mathbf{q}) + \Theta_{22}^{-1}(\mathbf{q})).\end{aligned}\quad (24)$$

At this point, we need to transform $\langle \vec{\phi}(\mathbf{x}_1), \vec{\psi}(\mathbf{x}_2) \rangle_{\mathbf{q}}$ back into real coordinate space. Both terms in the cross-correlation function take the form

$$\frac{1 + a^2 \mathbf{q}^2}{1 - c(1 + a^2 \mathbf{q}^2)} = \frac{(1 + a^2 \mathbf{q}^2)/ca^2}{1/a^2(1/c - 1) - \mathbf{q}^2}, \quad (25)$$

where $c = \Theta_{11\theta} \sigma^2 \beta / 2$. Each term, of course, is led by a complicated constant (independent of $\mathbf{q}$, but dependent on other model parameters) that we omit for the purpose of simplifying our analysis. The function in Eq. (25) has two simple poles at $\mathbf{q} = \pm i \sqrt{1/a^2(1/c^2 - 1)}$. Completing a contour integral around the positive pole in the complex plane, we have the relation

$$\begin{aligned}\langle \vec{\phi}(\mathbf{x}_1), \vec{\psi}(\mathbf{x}_2) \rangle \propto & \exp(-\sqrt{1/a^2(1/c^2 - 1)} \mathbf{x}) \\ = & \exp(-\mathbf{x}/\xi),\end{aligned}\quad (26)$$

where $\mathbf{x} = \mathbf{x}_1 - \mathbf{x}_2$ and, in the style of Ornstein and Zernike, ξ represents the $\vec{\phi} - \vec{\psi}$ correlation length for the system. Again, since the full correlation function for this system is quite complicated, we will focus our analysis on this correlation length. Inserting the value of c into the expression for ξ , we see that

$$|\xi| = \frac{a}{\sqrt{2kT/\sigma^2 \cos \theta - 1}}. \quad (27)$$

As a first observation, we can note from Eq. (27) that as $\sigma \rightarrow 0$ and/or $\beta \rightarrow 0$, $|\xi| \rightarrow 0$. These limits make intuitive sense: since ξ represents a cross-correlation length, it should go to zero when $\sigma \rightarrow 0$ and $\vec{\phi}$ disappears; all vectors, of course, should become uncorrelated as $T \rightarrow \infty$.

A notable feature of this correlation length is the divergence that arises when parameters are set such that $2kT/\sigma^2 \cos \theta = 1$. We argue here that this divergence occurs

in an area of parameter space that our model cannot describe, and should be ignored. For the denominator to remain above the divergence, our parameters must be set such that $2kT > \sigma^2 \cos \theta$. Remembering that $\cos \theta \leq 1$, we replace $\cos \theta$ with 1 in determining our bound. We now have the condition that

$$kT > \sigma^2/2. \quad (28)$$

Provided that $kT > \sigma^2/2$, the correlation length does not diverge. Recall that our expansion parameter used for perturbation theory took the form $\beta\sigma^2$, and from that we derived the expected model validity condition

$$kT > \sigma^2/b,$$

where b was a parameter of order one. In the case of the correlation length, it appears that the model remains valid for a value of $b \approx 2$, beyond which singularities and divergences appear.

Constraining kT , σ , and θ to the above-designated area of parameter space, we see that the magnitude of the correlation length is a well-behaved function. Figure 8 shows $|\xi|$ plotted versus θ at $kT = 0.6$ for various values of the disorder standard deviation σ . As can be seen from the curves at $\sigma = 0.8$ and $\sigma = 1$, the θ regime in which an entropy minimum appears seems to correspond (though not exactly) to the area of non-trivial $|\xi| > 1$ correlation length. This observation suggests a pleasing picture for our theory: increasing disorder at the surface induces a non-trivial $\phi - \psi$ correlation length, which manifests itself in a loss of configurational diversity (i.e., entropy) at the model interface. Beyond approximately $\theta = \pi/4$, correlations with the disordered field are smaller and seemingly insufficient to disrupt $\psi - \psi$ interactions. Bulk processes then dominate at the surface, and little loss in entropy is observed. One can also see a pleasing synergy between the cross-correlation lengths (Figure 8) and the phase diagram (Figure 6): the values of θ for which $|\xi|$ is the

FIG. 8. Magnitude of the correlation length versus model angle θ at various values of the field standard deviation σ . Temperature is fixed at $T = 0.6$. The area in which the correlation length is non-trivial (i.e., greater than 1) corresponds loosely with the parameter range in which the entropy was seen to be substantially reduced by disorder.

largest correspond to the areas of the phase diagram in which the field-induced phase emerges from entropic freezing.

With these results in mind, we need to discuss the interpretation of the $\vec{\phi} - \vec{\psi}$ correlation length we calculated under the scope of the approximations made in doing so.

The low momentum approximation ($\cos \mathbf{q} \approx 1 - \mathbf{q}^2$) implies that our model can only describe correlations that result from interactions at small $\mathbf{q}$. As we expect only the low-momentum Goldstone-like modes of the system to impact correlation behavior, however, this approximation is likely justified. The significance of the diagonal Γ approximation, while difficult to gauge from a theoretical standpoint, will likely be evident from the theory's relative agreement with Monte Carlo calculations.

Discerning the effects of invoking translational invariance, however, requires more thought. Rigorously, setting both $\delta(\mathbf{x}_1 \cdot \mathbf{x}_0)$ and $\delta(\mathbf{x}_2 \cdot \mathbf{x}_0)$ to unity implies that both $\mathbf{x}_1$ and $\mathbf{x}_2$ are on or adjacent to the system's embedded plane. When calculating $\langle \vec{\phi}(\mathbf{x}_1), \vec{\psi}(\mathbf{x}_2) \rangle$, the approximation for $\mathbf{x}_1$ is necessary: if $\mathbf{x}_1$ were not on the embedded plane, $\vec{\phi}$ would be zero and the correlation behavior would be trivial. Still, the field $\vec{\psi}$ described by the correlation function is rigorously restricted to be on or near the embedded surface. However, we can argue that $\langle \vec{\phi}(\mathbf{x}_1), \vec{\psi}(\mathbf{x}_2) \rangle$ captures more general behavior, as follows. The bulk field $\vec{\psi}$ is itself truly translationally invariant. Given that the field $\vec{\phi}$ is fixed at a point $\mathbf{x}_1$ on the plane, the $\vec{\psi}$ field should be agnostic to whether or not the coordinate $\mathbf{x}_2$ of $\vec{\psi}$ lies on the plane or off of it. In a sense, since the correlation function depends only on two points, only the relative difference between those two points matters, and translational invariance can be used. This argument breaks down, of course, when the correlation function is considered at higher than the two-point level.

Though the “near-plane” approximation is pervasive in this study, the correlation length, and its concomitant properties, can at least describe aspects of cross-correlation at arbitrary distances from the embedded surface. Since both interfacial and total correlation functions can be calculated from Monte Carlo data, our later simulations will provide a good avenue to test this claim.

B. Theory in three dimensions

While the above results are interesting from a physical standpoint, a biophysicist studying properties of water is primarily interested in the ($m = 3, n = 3$) case of the model. As mentioned in the Introduction, interfacial water in three dimensions plays a role in driving a myriad of biophysical phenomena related to protein folding and other processes.

The general phase-shifted model in the ($m = 3, n = 3$) Heisenberg regime is difficult to derive under our framework, as three-dimensional configurations will no longer be “frame invariant”; to be well-defined, the rotation matrix $\Theta(\mathbf{x}_1, \mathbf{x}_2)$ would have to rotate vectors relative to a reference coordinate system. Representation of the full $\Theta(\mathbf{x}_1, \mathbf{x}_2)$ kernel thus presents a challenge, as rotation now depends only on relative angles between vectors. The introduction of an inverse cosine function, which addresses this problem in our Monte Carlo

simulations, unduly complicates the analytical theory. We reserve a general solution for the three-dimensional model, if tractable, for future work.

However, we can study the properties of our model in three dimensions in one simple case: when vectors are subjected to no phase shift at all and pairwise anti-parallel interactions are favored. In this circumstance, the angular part of the kernel, Θ_A , can be represented by an identity matrix, giving a model analogous to the $\theta = 0$ model in two dimensions. Plugging a 3×3 identity matrix into Eqs. (6), (8), and (10)–(14), we have that

$$Z_{ann} = \frac{1}{\beta^{3/2} \sqrt{\det \Gamma(\mathbf{x}_1, \mathbf{x}_2)}} \quad (29)$$

and

$$\Gamma(\mathbf{x}_1, \mathbf{x}_2) = (\delta(\mathbf{x}_1 - \mathbf{x}_2) \mathbf{I} - \frac{1}{2} \sigma^2 \beta \times \mathbf{I}) \delta(\mathbf{x}_1 \cdot \mathbf{x}_0) \delta(\mathbf{x}_2 \cdot \mathbf{x}_0). \quad (30)$$

In matrix form, the angular portion of Γ is given by

$$\Gamma = \begin{pmatrix} 1 - \frac{1}{2} \beta \sigma^2 & 0 & 0 \\ 0 & 1 - \frac{1}{2} \beta \sigma^2 & 0 \\ 0 & 0 & 1 - \frac{1}{2} \beta \sigma^2 \end{pmatrix}.$$

Keeping in mind the spatial diagonalization carried out in the two-dimensional case, we can easily evaluate this determinant, yielding

$$\det \Gamma = 1 - \frac{3}{2} \beta \sigma^2 + \frac{3}{4} \beta^2 \sigma^4 - \frac{1}{8} \beta^3 \sigma^6. \quad (31)$$

We thus arrive at a final expression for Z_{ann} :

$$Z_{ann} = \frac{1}{\beta^{3/2} \sqrt{1 - \frac{3}{2} \beta \sigma^2 + \frac{3}{4} \beta^2 \sigma^4 - \frac{1}{8} \beta^3 \sigma^6}}. \quad (32)$$

We can calculate standard thermodynamic quantities from this partition function using the same Eqs. (16)–(18). Figure 9 shows the annealed average entropy plotted as a function of kT for the two- and three-dimensional models under the conditions $\theta = 0$ and $\sigma = 0.9$. As is clear from the figure, the three-dimensional entropy is quite similar to that derived in the two-dimensional case. The three-dimensional model entropically “freezes” just as it does in the two-dimensional picture; the freezing transition in three dimensions, however, occurs at a higher temperature than in two dimensions for $\sigma \leq 1$. Based on this observation, we predict that, for models that do freeze, freezing will occur at higher temperatures in the Heisenberg regime than those observed in the XY regime. This argument is intuitive from a physical standpoint, as a much greater “volume” of the bulk field interacts with the disordered interface in the three-dimensional case. (Volume, here, is generalized to one and two dimensions for the two- and three-dimensional systems, respectively.) As σ becomes large and $\phi - \psi$ interactions become dominant, the three-dimensional model is thus affected by the disorder to a greater extent, and freezing can occur at higher temperatures.

With respect to cross-correlation properties, we note that, under the approximations discussed above, the cross-correlation length in two dimensions depended on only one

FIG. 9. Entropy versus T for two- and three-dimensional vector field models at $\theta = 0$ and $\sigma = 0.9$. As determined by the first energy at which the entropy hits zero, the 2D model freezes at $T \approx 0.67$, while the 3D model freezes at $T \approx 1.05$. In general, we predict that freezing energies in the Heisenberg regime will be higher than those observed in two dimensions.

diagonal component of the matrix Γ^{-1} . If we make the same approximations in the three-dimensional case, the residues of Γ^{-1} 's diagonal components do not change (given the interpretation of θ as a relative angle phase shift). We predict, thus, that while the form of the correlation functions will be different in the Heisenberg regime, the cross-correlation lengths for phase-shifted three-dimensional systems should be very similar to those predicted for two dimensions.

To recapitulate the ideas from this section, we predict that three-dimensional models will exhibit similar freezing properties to those observed in two dimensions, and we suggest that the same correlation properties seen in two dimensions will give rise to freezing transitions at higher temperatures in the Heisenberg regime.

C. Monte Carlo calculations

As with any simple theory, comparison to some experiment or simulation is important both for validating results and providing feedback for interpretation. To validate our analytical theory against simulation, we have performed Monte Carlo calculations on discrete vector field analogs of the systems described above. The relative agreement between observables of our theory and those calculated from simulations (particularly, the entropy and the $\phi - \psi$ cross correlation length) will be used to assess the validity of our model.

To set up Monte Carlo simulations in two dimensions, two-component vectors representing the bulk ψ field were placed on a small 7×7 square lattice, emulating previous studies.^{28,34} Each component of the randomly distributed vector field ϕ was drawn from a Gaussian distribution with standard deviation σ , and the ϕ vectors were allowed to interact with neighboring ψ vectors to their right. To simulate

annealed disorder, the ϕ vectors were redrawn from their distribution every 100 Monte Carlo steps. Periodic boundary conditions were introduced in the axial direction (parallel to the field plane) only.

In order to include phase shifts in our simulations, we introduce the same parameter θ that rotates one vector in each pair-interaction. The energy for the lattice is then defined as the sum of nearest-neighbor dot products, summed over all vectors on the lattice and corrected for the parameter θ :

$$E_{\text{configuration}} = \sum_{i,j,k,m|_{nn}} \frac{1}{2} \cos((\theta_{i,j} - \theta_{k,m}) - \theta) + A|_{j=1} \cos(\theta_{i,j} - \Phi_k), \quad (33)$$

$$A|_{j=1} = \begin{cases} |\phi_i| & \text{if } j = 1 \\ 0 & \text{otherwise,} \end{cases}$$

where $\theta_{i,j}$ represents the angle of the vector $\psi_{i,j}$, Φ_k represents the angle of the vector ϕ_k , and the notation $i, j, k, m|_{nn}$ indicates that the sum is restricted to nearest neighbors (including axial periodic images). The indices i, j, k , and m run over all lattice points. The notation $A|_{j=1}$ indicates that vectors adjacent to the disordered ϕ field will interact with that field proportional to $|\phi|$, while all other vectors only interact in the bulk environment.

Simulations were allowed to proceed with moves based on the standard Metropolis criterion, and each individual calculation was run for 1×10^8 Monte Carlo moves. The simulations were deemed to be “at equilibrium” after 5×10^7 Monte Carlo moves (approximately 1×10^6 Monte Carlo moves per spin), after which configurations were recorded for another 5×10^7 steps so that equilibrium quantities could be calculated. Properties were calculated down to a bath energy of $kT = 0.2$, below which convergence times became prohibitive.

Sample equilibrium configurations from simulations of the $\theta = 0$ and $\theta = \pi$ models at $kT = 0.2$ and $\sigma = 1$ are given in Figure 10. Note that, based on the structure of the Hamiltonian, the $\theta = \pi$ model represents the traditional X-Y model in which spins become aligned at low temperature. The disordered field ϕ , surrounded by a bold border, can be seen disrupting local order in both configurations shown.

FIG. 10. Sample equilibrium configurations from Monte Carlo simulations of the (left) $\theta = 0$ model and (right) $\theta = \pi$ model on a 7×7 lattices. System parameters are set at $kT = 0.4$ and $\sigma = 1$. The disordered field ψ , here represented as a second vector field outlined by a box, can be seen at left in each configuration. Toroidal periodic boundary conditions were enforced in the axial direction only.

The emergence of quasi-order can be seen in the $\theta = \pi$ configuration, where bulk ψ vectors are nearly completely aligned.

As mentioned above, we will calculate two main observables to be used to compare to theory: the entropy and the $\phi - \psi$ correlation length. Theoretical expressions for both properties were derived in Secs. III A 2 and III A 3. From Monte Carlo data, the $\phi - \psi$ correlation function was calculated in a straightforward manner

$$\langle \phi, \psi \rangle(\mathbf{x}) = \frac{1}{N} \sum_{i,j,k} \phi_{i,j}(\mathbf{x}) \cdot \psi_k(\mathbf{x}), \quad (34)$$

where the average is computed for each discrete $\mathbf{x}$ over all N vectors $\phi_{i,j}$ and ψ_k that are $\mathbf{x}$ lattice spacings apart. Distances were based on the so-called “taxi cab” or “Manhattan” metric, wherein the distance between two points is measured as the sum of orthogonal coordinate distances. The product notation at right in Eq. (10) indicates a simple dot product between the vectors in question.

A cross correlation length was extracted from the above correlation function through least-squares fitting to a two parameter, single exponential equation $\langle \phi, \psi \rangle = A \times \exp(-x/\xi)$. Here, A represents the amplitude of the exponential and ξ represents the desired correlation length. Fits were calculated to the magnitudes of each correlation function to facilitate comparison between models. Figure 11 provides an example of a correlation function and its respective exponential fit for the $\theta = \pi$ model at $kT = 0.5$.

Interfacial entropies were calculated from Monte Carlo data by binning the equilibrium samples in configurational space, where each vector’s state (restricted to the first column of ψ vectors) was defined by its standard angle quadrant. Bin probabilities were obtained by normalizing the bin populations to sum to unity, and the entropy was computed from this distribution using the Gibbs Formula:

$$S = -k \sum_i p_i \log p_i, \quad (35)$$

FIG. 11. Exponential fit (solid line) to $\phi - \psi$ correlation function calculated from Monte Carlo simulation of $\theta = \pi$ model (data points). The correlation length ξ used to compare to theory is represented by the decay constant of a single exponential fit with amplitude A : $\langle \phi, \psi \rangle = A \times \exp(-x/\xi)$.

where the sum runs over all bins and p_i represents the probability of a particular bin. To compute an annealed average over the disorder, we need to normalize the entropy by an estimated “number” of realizations for the disorder. To do so, we use the differential entropy of the Gaussian distribution, given by the formula

$$S_G = \frac{1}{2} \log(2\pi e\sigma^2). \quad (36)$$

Exponentiating this Gaussian entropy, we find that our final expression for the annealed average entropy is given by

$$S_{ann} = -\frac{k}{\sqrt{2\pi e\sigma^2}} \sum_i p_i \log p_i. \quad (37)$$

Since, for small standard deviations, the differential entropy of the normal distribution becomes negative, we only normalize annealed entropies for which the Gaussian differential entropy is greater than zero.

In three dimensions, three component vectors representing the ψ field were placed on a $7 \times 7 \times 7$ lattice. The three components of vectors representing the ϕ field (placed on a 7×7 lattice) were again drawn from a Gaussian distribution with standard deviation σ ; ϕ vectors were redrawn every 100 Monte Carlo steps. Toroidal periodic boundary conditions were enforced in the two directions coplanar with the random field plane.

The Hamiltonian in three dimensions is represented as follows, extended naturally from the two-dimensional case:

$$E_{configuration} = \sum_{i,j,k,m,l,o|_{nn}} \frac{1}{2} \cos(\arccos(\psi_{i,j,k} \cdot \psi_{m,l,o}) + \theta) + A|_{j=1}(\psi_{i,j,k} \cdot \phi_{m,l}),$$

$$A|_{j=1} = \begin{cases} 1 & \text{if } j = 1 \\ 0 & \text{otherwise,} \end{cases}$$

where i, j, k, m, l , and o run over all lattice points and the notation $i, j, k, m, l, o|_{nn}$ indicates that the sum is restricted to nearest neighbors (including axial periodic images). The notation $A|_{j=1}$ again indicates that vectors adjacent to the disordered ϕ field will interact with that field proportional to $|\phi|$, while all other vectors only interact in the bulk environment. The angle parameter θ here represents a relative phase shift between two vectors, where the angle between two vectors is now determined by the inverse cosine of their dot product.

The convergence criterion was relaxed slightly for three-dimensional Monte Carlo runs: systems were equilibrated for 3.5×10^7 Monte Carlo moves (approximately one hundred thousand Monte Carlo moves/spin), and observable properties were calculated from configurations recorded during an additional 3.5×10^7 accepted moves. Figure 12 shows a sample equilibrium configuration from the $\theta = \pi$ model at $kT = 0.4$ and $\sigma = 1$.

Correlation lengths from the three-dimensional data were calculated using the same procedure as in the two-dimensional case. In order to calculate interfacial entropies,

FIG. 12. Sample equilibrium configuration from Monte Carlo simulations of the $\theta = \pi$ model in three dimensions on a $7 \times 7 \times 7$ lattice. System parameters are set at $kT = 0.4$ and $\sigma = 1$. The disordered field ϕ , represented in bold with lattice markers, can be seen closest to the configuration's y axis. Toroidal periodic boundary conditions were enforced along the y axis and z axis directions only.

configurations were binned as above, but now defining vector states (here, for the first plane of vectors) with standard angle octants. Entropies were then calculated using Eqs. (35)–(37).

D. Monte Carlo validation – The X-Y regime

Monte Carlo calculations in two dimensions were completed as described above over a volume in parameter space described by $0.2 \leq kT \leq 1$, $0 \leq \sigma \leq 1$, and $0 \leq \theta \leq \pi$. Entropies and cross-correlation lengths were calculated for each data set (comprised of 5×10^7 equilibrium configurations) using the protocol given previously. To facilitate evaluation of the arguments about translational invariance and correlation functions, we introduce two different types of correlation lengths. “Interfacial” cross correlation lengths were computed by calculating averages over only the first row of vectors in the ψ lattice (the second row overall), while “total” cross correlation lengths were averaged over all available vectors.

Figures 13 and 14 illustrate example comparisons of Monte Carlo data with predictions from the analytical model.

As a general observation, Monte Carlo data collected under conditions which violate Eq. (28) do not exhibit divergent correlation lengths, supporting the argument that such divergences are artifacts of the theory's approximations. Agreement with simulation under conditions in which the analytical correlation length diverges is, as a result, poor.

In areas of parameter space for which correlation lengths are well behaved, however, the agreement between theory and simulation is reasonable. Figure 13 shows the interfacial entropy versus θ curves predicted by the theory and calculated through simulation data. Qualitatively, the two curves are similar: the theory predicts the general shape of the curve and identifies the location of the entropy maximum nearly exactly.

FIG. 13. Comparison of interfacial entropy versus θ curves calculated through Monte Carlo simulations (right) with that of analytical theory (left) for $\sigma = 0.9$ and $kT = 0.6$. In general, the theory captures major aspects of the Monte Carlo entropy curve, including the location of the entropy maximum. While the Monte Carlo shows the $\theta = \pi$ model to have the least entropy, the models in the $\theta = 0$ to $\theta = \pi/4$ regime experience the greatest entropy reduction induced by the field. Inset: Entropy at $\sigma = 0$ for models at $kT = 0.6$. As indicated by the curve, the models in the small θ area experience the greatest reduction in entropy.

Monte Carlo entropies, it should be noted, cannot go below zero and take relatively large positive values due to finite size effects.

The Monte Carlo data do indicate that the entropy of the $\theta = \pi$ model is less than that of the $\theta = 0$ model. This decreased entropy, however, is likely due to the quasi-order seen in the bulk $\theta = \pi$ model rather than a disorder-induced effect. As evidence for this claim, the inset in Figure 13 shows the zero-disorder interfacial entropies for each model calculated from the Monte Carlo. The $\theta = \pi$ indeed has a drastically lower entropy than any other model in the absence of disorder. By contrast, the analytical theory predicts the same zero-disorder entropy over all models. The Monte Carlo seems to capture a low temperature bulk effect the analytical theory is not intended to encompass. Given the two high temperature approximations included in the theory (with respect to the Gaussian approximation and perturbation theory), we indeed

cannot expect our model to describe the low temperature phase of the XY model. Our models near $\theta = 0$ do, however, show a much greater field-induced entropy reduction than does the $\theta = \pi$ model. The theory and simulation agree in predicting that models at small θ are impacted by the random field to the greatest extent. Similar qualitative agreement between entropy curves was seen for other combinations of parameters in the $kT > \sigma^2/2$ regime.

Figure 14 shows a comparison between correlation length magnitudes predicted by theory and calculated through Monte Carlo. The horizontal line is included at $|\xi| = 1$ for reference. The area left of each vertical line, from left to right, corresponds to the area of parameter space that is frozen and frustrated but not frozen, respectively, as indicated by the presence entropy minima. Additionally, the red crosses correspond to the interfacial correlation length, while the blue dots indicate lengths calculated from the full correlation function. Note that the temperature is higher than the transition temperature for high- θ freezing (see Figure 7).

As can be seen from the data, the correlation lengths predicted by theory agree qualitatively with those calculated from Monte Carlo data. Though the values do not agree exactly, the analytical theory seems to have correctly predicted the trend in the θ dependence of the correlation length. Again, the Monte Carlo quantities do not approach zero, likely due to finite size effects; in the small θ regime, the theory even seems to have predicted total correlation length values with some accuracy. Again, similar qualitative agreement was seen for other well-behaved combinations of parameters.

Given that the analytical theory predicted the total correlation lengths reasonably well, we can conclude that our arguments about the effect of the delta functions on the correlation function have some validity. The interfacial correlation length actually agrees to a lesser extent with the theory than the total correlation length, possibly due to the interface's inherently poorer statistics. In general, however, we observe qualitative

FIG. 14. Comparison of Monte Carlo data (data points) and analytical predictions (solid line) of $|\xi|$ versus θ at $\sigma = 0.9$ and $kT = 0.6$. Crosses indicate interfacial correlation functions, while dots correspond to correlation functions calculated over all vectors. A horizontal line is placed at $|\xi| = 1$ for reference; the area left of each vertical line, from left to right, corresponds to the area of parameter space that is frozen and frustrated but not frozen, respectively. Agreement with theory, though not exact, is good for both interfacial and total correlation lengths.

agreement between theory and simulation for both entropy and cross-correlation lengths.

E. Monte Carlo validation – The Heisenberg regime

In three dimensions, we completed Monte Carlo calculations over a volume of parameter space described by $0.4 \leq kT \leq 1$, $0 \leq \sigma \leq 1$, and $0 \leq \theta \leq \pi$. Entropies and correlation lengths were again calculated using the protocol given above, in this case averaged over 3.5×10^7 equilibrium configurations.

Figure 15 shows interfacial entropies as a function of θ for three models at $\sigma = 0.9$ in three dimensions. To preserve scale, the values for $\theta = 3\pi/4$ and $\theta = \pi$ are placed in the inset at lower right. As the figure indicates, entropies for three-dimensional systems are generally lower than those for two-dimensional analogs. This observation supports our prediction that three-dimensional systems are able to “freeze” at higher temperatures than two-dimensional systems (i.e., that three-dimensional systems are affected to a greater extent by the random field). The trends in entropy versus θ are very similar, however, for two and three-dimensional models, with an entropy maxima occurring at intermediate θ . Models near $\theta = 0$ again experience the greatest entropy reduction when subjected to a random field, suggesting that disorder has the largest impact at $\theta \approx 0$ in both two and three dimensions. The extremely low entropy in the $\theta = \pi$ case (where spins are encouraged to be parallel) is likely again to be a consequence of bulk order effects that the analytical theory cannot capture in its entropy expression.

Figure 16 shows a comparison between cross-correlation lengths calculated from Monte Carlo data in three dimensions and those predicted in the two-dimensional case. To reiterate, we predicted above that correlation lengths should

FIG. 15. Interfacial entropies calculated from Monte Carlo data collected in three dimensions at $\sigma = 0.9$. Entropies for models at $\theta = 3\pi/4$ and $\theta = \pi$ are placed in the inset to preserve scale. In general, entropies in the three-dimensional case are lower than in the two-dimensional models; trends in entropy versus θ , however, are similar in both cases. Most notably, models with θ near 0 experience the greatest entropy reduction induced by the random field in both two and three dimensions.

FIG. 16. Comparison of three-dimensional Monte Carlo data (data points) and two-dimensional analytical predictions (solid line) of $|\xi|$ versus θ at $\sigma = 0.9$. Correlation lengths calculated for three-dimensional systems are largely in agreement with those predicted in the two-dimensional regime.

be very similar for two- and three-dimensional systems. Figure 16 seems to support this prediction, as cross-correlation lengths computed from the Monte Carlo data agree qualitatively (and, to some extent, quantitatively) with analytical correlation lengths predicted in two dimensions.

Looking back to our Hamiltonian, we can suggest an explanation for the trends seen in entropy and correlation length (in both two and three dimensions) by citing simple physical principles. For a pair of vectors in models at $\theta = 0$ and $\theta = \pi$, only one optimal interaction exists: fixing one vector in space, a second vector must move into an antiparallel (for $\theta = 0$) or parallel (for $\theta = \pi$) arrangement to minimize the configuration’s energy. However, this property does not hold for models with intermediate θ . Once one vector is fixed in two dimensions, a second vector can move to one of two positions and still minimize the pairwise energy. The number of optimal vector positions becomes infinite in three dimensions, where a whole cone (converging to a disc, for $\theta = \pi/2$) of minimizing interactions become possible once one vector’s position is fixed.

As such, it is sensible that the disordered field has a greater impact on models near $\theta = 0$ and $\theta = \pi$. When θ is intermediate, interactions between the ϕ and ψ fields can often be accommodated simultaneously, as vectors can rotate through many energetically minimal positions. Entropy at the interface can be retained in this fashion, and cross-correlations are diminished. By contrast, bulk vectors under conditions near $\theta = 0$ and $\theta = \pi$ have far fewer options for energy minimization. When a particularly favorable $\phi - \psi$ interaction arises, thus, that interaction is favored at the expense of the bulk field. A loss in interfacial entropy results, and $\phi - \psi$ correlations are significant. The smaller correlation lengths for models near $\theta = \pi$ could result from the emergence of the cooperative (quasi-)ordered phases of the X-Y and Heisenberg models, which would inherently be less susceptible to frustration at one interface. Figure 17 provides an illustration of these effects.

FIG. 17. Illustration of fundamental entropic and $\phi - \psi$ correlation effects as inferred from analytical theory and Monte Carlo calculations (illustrated in three dimensions). The horizontal line indicates the trivial lattice spacing, $a = 1$. For models with intermediate θ , pairwise interactions can be satisfied by vectors placed anywhere on the conical surfaces shown in the figure. These many possible optimal orientations allow for better entropy retention in the bulk phase when a strong interfacial random field is introduced, and cross correlation effects are diminished. However, at $\theta = 0$ and $\theta = \pi$, only one optimal orientation between two vectors exists. In these cases, the random field is thus more disruptive to the bulk field, as indicated by increased cross correlations. It is likely that the emergence of bulk order near $\theta = \pi$ decreases the impact of the random field on those models.

F. Assessment as a model for frustrated water

We have yet to mention the possible implications this theory might hold for understanding water's role in biophysical systems. At this point, our theory is completely agnostic to the physical system it describes. We have described the interaction between two arbitrary vector fields (one with harmonic self-interaction, and the other subjected to disorder) at a planar interface, and we have derived the phase and correlation behavior that results from this interaction. Therefore, we would expect our results to be valid for any physical field (placed at a Gaussian-disordered interface) that is well-described by harmonic self-interaction.

In the context of water, we have mentioned previously that a dipole field would serve as a good candidate for a physical field of interest. Indeed, harmonic models of (polarizable) polar fluids use dipole moment fields with Gaussian interactions to describe a fluid's equilibrium properties, to good agreement with experiments.⁴⁰ In these models, complicated operators like angle-dependent pair-distribution functions and polarizability tensors act as the kernels in the dipole field's self-interaction. As such, properties like the optimal phase-shift for the vector field would be diverse and would vary spatially. One thus might expect to see a broad distribution of phase shifts in real polar fluids (e.g., water), and these phase shifts would depend on local solvent properties.

In a sense, our phase-shift kernel, Θ , operates as a simpler surrogate to the physically rigorous but complicated operators from theories of polar fluids. Each value of θ might represent an optimal local orientation of a dipole field. With interfacial disorder, our theory suggests that frustration arises in the bulk vector field when the phase-shift is either small ($\theta \approx 0$) or large ($\theta \approx \pi$). Accordingly, we might expect regions of a water dipole field that exhibit small or large phase shifts to be susceptible to frustration when placed at a disordered

interface. Nearly parallel or nearly anti-parallel regions in the dipole field, thus, might act as signatures of frustrated phases in polar fluids.

We also noted previously that, owing to the necessity for Gaussian statistics, our bulk vector field would likely correspond to a slightly coarse-grained physical field. The literature employing coarse-grained water models to describe hydrophilicity, hydrophobicity, and dewetting phenomena is well developed. In particular, coarse-grained density field-based approaches have succeeded in capturing the role fluctuations play in the hydrophobic effect and other processes.^{41,42} To some extent, a number density field is a first-order "monopole" representation of a system, as it depends only on particle positions. Dipole (and even quadrupole) fields are natural higher order extensions of the density field, as they describe more detailed relationships between position and charge. Previous models claim that these higher order effects are implicitly accounted for by density field parameters.^{41,42} Our coarse-grained dipole field, however, would capture these higher order effects directly. It would be interesting to use a dipole fields in tandem with density fields to see if new information about frustration-related processes could be extracted.

However, framing our model in the context of this previous work by Chandler *et al.* requires us to mention an additional limitation of our theory. Under biological conditions, water exists close enough to its tricritical point that phase coexistence can play a considerable role in its physics at interfaces. In particular, near hydrophobic surfaces that do not interact strongly with water, a liquid-vapor coexistence forms that results in a depletion of density at the interface. Inclusion of coexistence behavior is thus essential for describing the hydrophobic effect and other water behavior at hydrophobic interfaces.

To describe a liquid-vapor coexistence from a field theoretic perspective, at least quartic interactions in the bulk field (here, ψ) are required to allow multiple free energy minima to arise. In keeping our theory fully integrable and simplifying the nature of the model interface, our model currently includes interactions only to the Gaussian level. As a consequence, the present theory would likely not be well suited to describing water at hydrophobic interfaces.

At polar interfaces, however, the water density is actually enhanced compared to bulk; as such, liquid-vapor coexistence near polar surfaces should have a muted effect on water behavior. In these cases, Gaussian fluctuations in the liquid should be sufficient to capture the important physics involved. We argue, thus, that our theory can provide a minimal model for frustrated water at polar biological interfaces. Indeed, our theory was never apt to describing water at inert surfaces, as complete bulk interactions remain available at the interface when σ is brought to zero. If σ is small, bulk liquid behavior dominates, and the interface effectively disappears instead becoming an inert surface. When the interfacial field (i.e., a dipole field for a polar surface) is large in magnitude, the interface again comes into play; our model should describe frustrated interactions in these instances quite well.

While our theory shows promise for providing phenomenological descriptions of water behavior, a perhaps more

tantalizing application lies in its use for analyzing fully atomistic molecular dynamics (MD) data of polar interfaces. As mentioned in the Introduction, explicit water MD simulations of the chaperonin GroEL pointed at interesting, non-bulk-like water behavior inside the chaperonin cavity.¹² A wide body of work featuring explicit water simulations of hydrophobic collapse and interfacial water behavior exists for other biophysical systems.^{43–48} However, connecting the microscopic, dynamical behavior one sees in MD trajectories to some sort of physical understanding is often a challenging task. Analysis of dipole field correlations at biological interfaces might provide a useful avenue for making such connections at a mesoscopic level.

One could imagine collecting MD data of water in explicitly represented biological systems and then computing coarse-grained dipole fields corresponding to the solvent (bulk vector field) and biomolecule (disordered field). One could then look for meaningful dipole correlations at the interface that would provide some structural or functional insight. In particular, since the interior surface of the closed GroEL complex is highly polar, ideas from our theory alone could go far in elucidating solvent structure in this system. For systems in which both hydrophobic and hydrophilic interactions are important, our theory could be used in tandem with density fields that could capture more complicated bulk phase behavior. In a related sense, one could also imagine using both density and dipole representations of solvent for clustering configurations in quantitative kinetic models of protein-water systems.^{49,50}

As with other theories of confined water, our model suggests that the disordering field-field correlations could reach to biologically relevant length scales. If we insert molecular-scale parameters for the arbitrary lattice spacing a , cross-correlation lengths in our theory can spread over a distance occupied by several water molecules. Given a strong enough random field, disorder can thus extend to the range necessary for impacting processes like protein folding that occur on the nanometer scale. We should note, however, that our theory subjects the bulk vector field to purely random disorder. Chemical structures at biological interfaces are decidedly not random, as such structures have been optimized by the rigors of evolution. It will be interesting to compare cross-correlations at evolved biological interfaces to those correlations seen at random interfaces. It is possible that evolution has amplified the interfacial correlations predicted by our random theory, so that some biological processes can be better mediated through disordered solvent interactions.

IV. CONCLUSION

In this study, we have used field theoretic techniques to derive a general model for the interaction of a bulk vector field and a disordered field embedded on a plane. We have analyzed the model in detail for the phase-shifted X-Y regime, and we have suggested what the model might look like in three dimensions. Given the qualitative agreement we see between theory and simulation in two and three dimensions, we can conclude that our analytical theory has some predictive value for characterizing frustration in phase-shifted

vector field models subjected to interfacial annealed disorder. We have also discussed how this theory might be connected to theories of confined water, and we have mentioned possible applications of this coarse-grained representation to understanding water in biophysical systems.

In the future, we would like to extend our analytical theory's embedded surface to possess a more complicated topology than that of a flat plane (e.g., through adding curvature to the surface). Additionally, we would like to extend the model to include interaction gradients that allow for longer than nearest-neighbor couplings, and we would like to include quartic and higher order interactions to describe phase coexistence in the bulk field, as discussed above. These alterations would be performed with the hope of moving toward a more complete description of confined, charge- and topography-frustrated water.

Integration of all of these features into a fully integrable field theoretic model is a daunting, if not an impractical, task. Certainly, theory at all levels will be necessary in the ongoing study of the biophysics of water.

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