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CHARGE FRUSTRATION, BICONTINUITY AND INTERFACES
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ABSTRACT

This paper reviews and discusses implications of the results obtained with the charge frustrated Ising model. It is a model of self-assembly for oil-water-surfactant mixtures. It applies to other systems as well.

Oil, water and surfactants

At normal temperatures, oil and water don't mix. On large length scales and away from criticality, the only structure that exists in this system is the oil-water interface. It's an Ising system. The addition of some surfactant, however, changes the physics. With the surfactant, the system self assembles, forming very many mesoscopic structures. The change in physics is due to frustration. The frustration follows from the constraint of stoichiometry. This constraint forces oil-like and water-like species to exist within a microscopic distance - the length of a surfactant molecule. On larger length scales, the entropic effects of this constraint are the same as the energetic effects of electroneutrality in a charge particle system. Stillinger and others have noted this apparent mapping.\textsuperscript{1-3} We have used it to motivate the charge frustrated Ising model for oil-water-surfactant mixtures.\textsuperscript{4,5}

The charge frustrated Ising model is characterized by one energy and two lengths. The energy is essentially the low temperature oil-water surface tension in the absence of surfactant. The two lengths are the correlation length of the oil-water system in the absence of surfactant, and the mean length of a surfactant molecule. Analysis of this minimalist model and comparison with experiment is reviewed in this paper. Since the reviewed material is well described in the primary literature,\textsuperscript{4-7} what I say now is appropriately brief.

Charge frustrated Ising model

The model has two binary variables: $s_i = \pm 1$, indicating whether lattice site $i$ is occupied by a polar or hydrophobic species, and $t_i = 1, 0$, indicating whether that species is or is not part of a surfactant (if it is not, the species corresponds to water or oil). One may imagine, for example, a cubic lattice with lattice spacing $a$. The symmetry of the lattice should be irrelevant, but
the microscopic length scale it introduces is significant. It corresponds to the correlation length of the oil or water phases in the absence of surfactant. It is a small length of the order of 2 to 3 Å.

The Hamiltonian of the charge frustrated model is

\[ \mathcal{H} = -J \sum_{ij} s_i s_j + \frac{1}{2} q^2 \sum_{i \neq j} \mu_i s_i s_j t_i t_j - \sum_i (h s_i + \mu_i) \]  \tag{1}

The primed double sum is over nearest neighbor pairs, and the coupling \( J \) is positive. The second double sum is the Coulomb term. Namely, \( v_{ij} \) is the inverse Fourier transform of \( 4\pi/k^2 \). Its strength is governed by the size of the charge \( q \). This charge is given by Stillinger’s formula \(^1\)

\[ q^2 = d/4\pi \beta \rho \Delta^2 \]  \tag{2}

where \( d \) refers to dimensionality, and \( \beta \) is the reciprocal temperature \( 1/k_B T \). The length \( \Delta \) is essentially the root mean square separation of polar and hydrophobic groups within a surfactant molecule, and \( \rho \) is the average bulk density of surfactant. The quantities \( h \) and \( \mu \) are the chemical potentials that govern the relative amounts of oil and water, and the concentration of surfactant. The charge depends upon surfactant concentration, i.e., \( \rho \). The model must therefore be treated self consistently.

The size of the ferromagnetic coupling, \( J \), can be estimated from the oil-water surface tension, \( \sigma \). Far from oil-water criticality,

\[ J \approx \sigma a^2 / 2 \]  \tag{3}

and at room temperature, \( \sigma \approx 0.1 k_B T \AA^{-2} \). Thus, the parameters characterizing the charge frustrated Ising model of oil-water-surfactant systems are all reasonably well known. This knowledge is of significance when using the model to explain experimental observations.

The Coulomb interactions favor anti parallel spins, the ferromagnetic interactions favor parallel spins. The charges will organize so that electroneutrality is maintained in volumes much larger than those circumscribed by a screening length. Debye’s formula for the screening length in this model is \( r_D = \Delta/\sqrt{6} \). If the amphiphilic surfactants are significantly longer than the lattice spacing, \( a \), the competing interactions will cause frustration. Spatially modulated phases may therefore follow.

In general, constraints have a corresponding electrostatic representation. The Coulomb interaction is the longest wavelength manifestation of the constraint.
Monte Carlo

Computer simulation provides an assessment of the possible structures that result from Coulomb frustration of the ferromagnetic Ising system. Figures 1 and 2 show typical configurations of equilibrated $d = 2$ Monte Carlo simulations. The pictured cases correspond to surfactant added to either pure water or pure oil. Thus in these cases, the self assembled structures are built from
Figure 2: Snapshots of some typical configurations of the charge-frustrated Ising model for various surfactant concentrations, at a higher temperature than those in Fig. 1. The concentration of charged particles is in (a) $\rho = 0.02/a^2$; in figure (b) $\rho = 0.04/a^2$; in figure (c) $\rho = 0.06/a^2$; and in figure (d) $\rho = 0.12/a^2$. This figure is taken from Ref. 4.

micelles or bilayers. The arrangements of micelles and bilayers look very much like complex fluid assemblies observed in Nature, including dense micellar liquids and oriented lamellar phases.

The Monte Carlo equilibration of these phases is not trivial. Standard single spin moves fail in this regard. The frustrated system quickly organizes, but it then fails to move further unless the clustered spins are displaced collectively.
Standard Monte Carlo converges to a quenched configuration, not a sequence of equilibrated fluid configurations. The pictures given in Figs. 1 and 2 were obtained from a Monte Carlo algorithm with collective moves designed specifically to simulate fluid self assembly.  

Bicontinuous microemulsions

In some situations, analytical analysis of the charge frustrated Ising model is particularly simple. A bicontinuous microemulsion is one such case. On a macroscopic scale, this type of material is a homogeneous mixtures of oil and water. On the microscopic scale, however, surfactant divides mesoscopic domains of oil and water. The separated domains percolate throughout the system. Surfactant interfaces are therefore ubiquitous.

The analysis of interface Hamiltonians is standard for treating systems that are extensive in interfaces. This approach, however, does not address issues such as the stability of the assembled interface and the role of molecular parameters such as surfactant length.

A field theoretic formulation of the charge frustrated Ising model has been used to treat bicontinuity in oil-water-surfactant mixtures. Here, the variables \( \{ t_i \} \) can be integrated out in a Gaussian approximation leaving a reduced Hamiltonian involving only the spins, \( \{ s_i \} \). For the case of equal volume fractions of oil and water, the reduced Hamiltonian is

\[
\hat{H} = -J \sum_{ij} s_is_j + \frac{1}{2}q^2 \sum_{i\neq j} L_{ij} s_is_j
\]  \hspace{1cm} (4)

where \( L_{ij} \) is the screened Coulomb interaction. It is the inverse Fourier transform of

\[
\hat{L}(k) = \frac{f\alpha/\Delta}{1 + \Delta^2k^2/6}
\]  \hspace{1cm} (5)

where \( f = 2\rho a^2 \Delta \) is essentially the volume fraction of surfactants. Widom's pioneering lattice model of microemulsions can be obtained as an approximation to Hamiltonian (4). Specifically, Widom's model coincides to a particular truncation of \( L_{ij} \) and a particular choice of the parameters \( q, \Delta \) and \( f \). The restrictions that lead to Widom's model, however, are without a molecular basis.

Teubner and others have used a random wave model to describe the structure of bicontinuous microemulsions. This model provides a picture from which the partition function for Hamiltonian (4) can be treated to a good
approximation. In particular, imagine expanding about a Gaussian reference Hamiltonian

\[ \mathcal{H}_G \approx (k_B T/2) \sum_{i,j} \psi_i G_{ij} \psi_j \]  

(6)

where \( s_i \) is determined by \( \psi_i \) through a local transformation

\[ s_i = c(\psi_i) \]  

(7)

One encounters such transformations, for example, in the field theoretic formulation of the Ising model.\(^{13}\) In that case, \( c(\psi) = \tanh(\psi) \), which is the specific form we use. In the random wave model, interfaces are constructed from a level clipping of a Gaussian field. This construction corresponds to taking \( c(\psi) \) as a step function. On length scales that are large compared to interfacial widths, differences between continuous and discontinuous transformations are physically inconsequential. For the purposes of relating the Gaussian model to the actual Hamiltonian, however, a step function is not acceptable as it is not invertible. An invertible transformation is required, however, to construct the Jacobian that relates the metric of \( \{s_i\} \) to that of \( \{\psi_i\} \). Provided the Jacobian exists, the partition function for Hamiltonian (4) can be estimated by perturbation theory expanding about the Gaussian reference.

A form of Hartree self consistent field theory can be carried out in this way. For quantitative results, it is important to impose upon the calculation the average effect of the hard spin condition

\[ \langle s_i s_j \rangle = 1 \text{ for } i = j. \]  

(8)

This imposition gives a mean spherical approximation. Its evaluation for the charge frustrated Ising model is remarkably simple, giving the following small wave vector expression for the spin-spin structure factor:\(^5\)

\[ S_k = \frac{1}{a^2 + c_1 k^2 + c_2 k^4} \]  

(9)

with

\[ a_2 = \frac{c^2}{4} \left( \frac{a^6}{16\pi^2 c_2} - \frac{c_1}{c_2} \right)^2 \]  

(10)

\[ c_1 = \beta \sigma a^4/2 - f a \Delta/6 \]  

(11)

\[ c_2 = f a \Delta^3/36 \]  

(12)
Figure 3: SANS spectra of $\text{D}_2\text{O}$-n-octane-$\text{C}_{12}\text{E}_6$ systems at varying surfactant volume fraction, $f$. Data is from Ref. 20 a) $f = 0.0566$, b) $f = 0.121$, and c) $f = 0.200$. The corresponding solid lines are the result of Eqs.(9)-(12), with $\sigma \approx 0.1 k_B T$ and $\Delta \approx 11 \text{Å}$. This figure is taken from Ref. 5.

Equation (9) is valid provided $k$ is small in comparison with $2\pi/\Delta$. This condition holds for most of the range of wave vectors probed in small angle neutron and x-ray scattering. The algebraic form of Eq.(9) was introduced phenomenologically by Teubner and Strey. The charge frustrated Ising model provides the molecular interpretation of the phenomenological coefficients. Comparison of theory and experiment is successful, as illustrated in Fig. 3. It is remarkable that frustration described by just two microscopic lengths, $a$ and $\Delta$, leads to separated domains of oil and water many times larger in size.

For wave vectors beyond the range considered in Fig. 3, or for describing interfacial fluctuations, Eq.(9) does not suffice. The transformed Gaussian field, however, remains useful. For the purpose of visualization, for example, a configuration of the Gaussian field can be generated by computer. The level surface of this field can then be rendered with computer graphics giving a
picture of a bicontinuous phase. This is the type of rendering done by Chen and coworkers.\textsuperscript{12} An example taken from our work is shown in Fig. 4.

Beyond the main peak, the structure factor of the bicontinuous microemulsion decays as $k^{-4}$. See Eq.(9). This power law is observed whenever narrow random interfaces fill a system.\textsuperscript{16} The converse is not necessarily true, however. Namely, while Eq.(9) holds, it is possible that interfaces can be broad, with widths comparable to the domain size. In other words, with enough surfactant, a microemulsion can be formed with largely diffuse regions of surfactant dividing oil and water. Such a material would not be microphase separated, in the traditional sense of the terminology. Calculations employing the charge frustrated model predict that some bicontinuous microemulsions exist in this way, with diffuse interfaces.\textsuperscript{7}
Metallic and insulating behaviors in liquids

The fact that charge frustration can lead to bicontinuous structure allows us to understand how this structure appears in a system that, at first thought, seems very different than oil-water-surfactant systems.

By computer simulation, Klein and coworkers have found a phase of metal-ammonia solutions that is bicontinuous.\(^{17}\) According to their simulation, electrons are microphase separated from the solution of ammonia molecules and metal ions. This bicontinuous structure characterizes the conducting phase of these solutions.

The connection between this result and charge frustration begins with an observation made by Alavi and Frenkel.\(^{18}\) They examined a version of Falicov and Kimball's itinerant electron model.\(^{19}\) At high enough density, Alavi and Frenkel found that a gas of ideal fermions will phase separate from a fluid of classical blockers. In essence, this phase separation occurs when the Fermi pressure overwhelms the pressure of the blocks, thus squeezing out the blocks. At lower fermion chemical potential, the fermions and blocks are mixed. In the mixed phase, the fermions are at low concentration, localized in voids. The mixed phase is insulating, and the separated phase is conducting.

Electrons are born into liquid ammonia by dissolving metal, like Li or Na. The electrons leave the metal atoms because the solvation energy of a metal ion out weights the ionization potential of the metal atom. The itinerant electrons thus formed experience a random field due to the disordered arrangement of ammonia and metal ions in the liquid. The field has regions of high potential (like the location of blockers) and regions of low potential (like the voids in the sea of blockers). At low concentration, the electrons will be localized in the largest regions of low potential energy. There are relatively few of these regions. Hence, due to the Pauli exclusion principle, only a few electrons can be accommodated in this way. As a result, phase separation would seem to occur at a high enough electron chemical potential, provided this chemical potential is below the threshold to extended states. This threshold is generally very high for electrons in polar liquids. Thus, the Alavi-Frenkel phase separation should be relevant.

Metal-ammonia solutions are complicated, however, by Coulomb interactions. Macroscopic separation of electrons from ions cannot occur as it would violate electroneutrality. Coulomb interactions will therefore frustrate the Alavi-Frenkel transition. Given the bicontinuous structure that is produced when Coulomb frustration alters the Ising transition, the bicontinuous structure discovered by Klein and his coworkers seems understandable. It is a possibility that merits quantitative study.
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References