Charge frustration in complex fluids and in electronic systems

Carlo Carraro
Department of Chemistry, University of California
Berkeley, California 94720-1460 USA

August 13, 2018

Abstract

The idea of charge frustration is applied to describe the properties of such diverse physical systems as oil-water-surfactant mixtures and metal-ammonia solutions. The minimalist charge-frustrated model possesses one energy scale and two length scales. For oil-water-surfactant mixtures, these parameters have been determined starting from the microscopic properties of the physical systems under study. Thus microscopic properties are successfully related to the observed mesoscopic structure.
1 Introduction

The physics of frustration underlies the behavior of many different physical systems. Competing interactions or unfavorable boundary conditions often frustrate the phase equilibrium of a physical system and play an important role in the formation of large interfacial structures or of topological defects. Examples include the domain walls in a magnetic system or in oil-water-amphiphile mixtures, the vortex lines in a type-II superconductor, or the entangled disclination lines in a metallic glass. At sufficiently low temperature, these defects can exist in an ordered state, such as the hexagonal vortex arrays of type-II superconductors, or the lamellar, hexagonal, and cubic phases of an amphiphilic mixture. At higher temperature, these ordered structures melt into disordered (liquid) phases, such as the vortex liquid phase of high temperature superconductors or the microemulsion phase of amphiphilic mixtures.

These disordered liquid phases behave differently than simple liquids. They retain a great deal of organization on mesoscopic scales, as is beautifully exemplified by small angle neutron scattering experiments on water-oil-amphiphile mixtures. The presence of order on scales that are much larger than molecular dimensions makes it difficult to explain experimental observations starting from the known molecular properties of the system. Recent progress in this direction has been possible using the idea of charge frustration\[1, 2\].

Charge frustration originates in the impossibility to separate opposite charges on macroscopic scales, due to the overextensive energy cost that such separation would entail. Thus, in a neutral Coulomb gas, charge neutrality is a local effect, and interactions have a finite range, \(\Delta\), of the order of the Debye-Hückel screening length.

Consider, for example, a two-component system in which short range forces favor phase separation. If the two components carry opposite charge, macroscopic phase separation cannot take place. Nevertheless, it is possible that the length scale over which charge neutrality is enforced, \(\Delta\), is much larger than the range, \(a\), of the forces which drive phase separation. In this case, the two-component system can find local rearrangements that minimize the short range repulsion while keeping overall neutrality on a length scale \(\Delta\). The compromise can be achieved, for example, by forming narrow interfaces separating mesoscopic domains. This arrangement is called microphase
separation. The material is homogeneous on large macroscopic scales, but phase separated on shorter mesoscopic scales.

In this paper, we study charge frustration in microemulsions and in some electronic systems. In microemulsions, which we discuss in Sec. II, charge frustration does not originate from the presence of unbound electric charge; rather, its origin is in the entropy reduction that stoichiometric constraints impose on an amphiphilic mixture. In Sec. III, we discuss metal-ammonia solutions, an electronic system where charge frustration is literally brought about by electric charge. Our conclusions are presented in Sec. IV.

2 Charge frustration in oil-water-amphiphile mixtures

Water and oil are immiscible fluids: when mixed, they phase separate into two almost pure components, divided by a narrow interface. The magnitude of the interfacial tension, of order 20 dynes/cm, is a measure of the strength of the hydrophobic interaction that drives the phenomenon of phase separation; the width of the interfacial region, of order the size of a water molecule, is a measure of its range. Thus, the phase diagram as well as the long wave length (Ornstein Zernicke) structure of the binary mixture can be described simply in terms of one characteristic energy parameter and one length scale. A detailed molecular description is indeed redundant and conveniently forgone in favor of a density field theory, with hamiltonian given by

$$\frac{H}{k_B T} = \int d^3 r \left( -\rho_w(\vec{r}) \log \rho_w(\vec{r}) - \frac{\rho_o(\vec{r})}{n_o} \log \rho_o(\vec{r}) + \sum_{ab \in \{w,o\}} \rho_a(\vec{r}) \frac{J_{ab}}{k_B T} (r-r') \rho_b(\vec{r'}) \right),$$

(1)

where $\rho_w$, $\rho_o$ represent water and oil densities, respectively, and the interaction matrix $J$ is characterized by a short range, $a$. An equally convenient representation can be given in terms of a spin 1/2 Ising model:

$$H = -\sum_{ij} J_{ij} s_i s_j - h \sum_i s_i.$$

(2)

Here, up (down) spins represent water (oil) density.

The addition of a small amount of surfactant molecules frustrates phase separation. This is because the polar head of a surfactant interacts more
favourably with the polar water molecules, while the hydrophobic tail of a surfactant is driven towards the oil phase. The presence of a covalent bond between head and tail of a surfactant implies that their amphiphilic tendency is satisfied if both water and oil phases can be found within a spatial range roughly equal to the length of a surfactant molecule. Thus, surfactants promote the formation of oil-water interfaces.

The presence of extensive interface (i.e., of amounts of interfacial area proportional to the number of surfactants) implies that an imaginary straight line through the amphiphilic mixture must thread many oil-water interfaces, a fact which is incompatible with macroscopic phase separation. Indeed, the mixture consists of a multitude of oil and water domains. It is microphase separated.

Small angle scattering experiments[3] show that the system is indeed ordered on mesoscopic scales, in the sense that there is a well defined domain size, which leads to oscillations in the long wave length structure factor. It is a challenge for theory to predict this domain size, starting from the knowledge of the chemical composition of the mixture.

Amphiphilicity is a molecular property, but phase separation is best described in terms of density fields. To successfully develop a theory of microphase separation, one must address the question: how do density fields "know" about molecules? To answer this question in a rigorous manner, one should a) define appropriate density fields, and b) integrate out the molecular coordinates in favor of the collective variables. Neither step is trivial.

An imaginative proposal for an approximate solution to this problem was put forward by Stillinger[4], who chose as collective variables the densities of hydrophobic and polar species; i.e., the natural variables in term of which the problem of phase separation is simple. However, this choice entails breaking up amphiphilic molecules into polar heads and hydrophobic tails. Stillinger further breaks up each head (tail) into $n_H$ ($n_T$) monomers, and assigns a polar density field, $\rho_H$, to the head monomers and a hydrophobic density, $\rho_T$, to the tail monomers. Disregarding the molecular nature of the mixture, the Hamiltonian would be as in Eq. (2.1). However, the interaction between density fields must reflect (at least on a mean field level) the covalent bond present in the molecules. Therefore, assuming that fluctuations in the head-
The tail mixture can still be described by Gaussian fields, one can write

$$\frac{H}{k_B T} = \frac{1}{2} \int d^3r \int d^3r' \sum_{ab} \rho_a(\vec{r}) \Omega_{ab}(r - r') \rho_b(\vec{r}'), \quad (a, b) \in (H, T),$$

(3)

but the interaction matrix \( \Omega_{ab} \) remains to be determined.

The appeal of Stillinger's work lies in the way it makes the connection between molecular variables and density fields, by comparing the intramolecular structure factor, which can be computed independently, in the low density approximation, starting from either molecules or densities. In terms of densities, one has

$$\Omega_{ab}^{-1}(\vec{k}) = \langle \rho_a(\vec{k}) \rho_b(-\vec{k}) \rangle.$$  

(4)

In terms of molecular coordinates, one finds

$$\langle \rho_a(\vec{k}) \rho_b(-\vec{k}) \rangle = \sum_{i \in a} \sum_{j \in b} \langle e^{i\vec{k} \cdot \vec{r}_i} e^{-i\vec{k} \cdot \vec{r}_j} \rangle \approx n_a n_b - \frac{k^2}{6} \Delta^{(2)}_{ab},$$  

(5)

where

$$\Delta^{(2)}_{ab} = \sum_{i \in a} \sum_{j \in b} \langle |\vec{r}_i - \vec{r}_j|^2 \rangle.$$  

(6)

This comparison enables one to identify the interaction matrix, which, along with the hydrophobic interaction, contains a Coulomb-like part:

$$\Omega_{HT}(\vec{k}) \approx \frac{3}{n_H n_T \Delta^{(2)} k^2},$$  

(7)

where

$$\Delta^{(2)} = \frac{\Delta^{(2)}_{HT}}{n_H n_T} - \frac{\Delta^{(2)}_{TT}}{n_H^2} - \frac{\Delta^{(2)}_{HH}}{n_T^2},$$  

(8)

is of order the mean square length of a surfactant molecule. A mapping of an amphiphilic mixture onto an electrolytic solution naturally ensues. Note that the effect of the Coulomb interaction is such that polar and hydrophobic densities attract, thus opposing phase separation. Hence the origin of charge frustration.

In spite of the apparent long range nature of the interaction matrix, the correlations in the system are in fact short ranged, as they must be in any fluid away from a critical point. The equivalent electrolytic solution is neutral, and the Coulomb potential is thus screened. An ion in a neutral
Coulomb gas is surrounded by an oppositely charged cloud of ions within a Debye screening length. Similarly, in an amphiphilic mixture, the presence of surfactant head (tail) density at a point implies the presence of an equal amount of tail (head) density within a distance of order the length of a surfactant molecule.

This observation is crucial in determining the way in which the elementary charge should be assigned in the electrolyte-amphiphile mapping. Indeed, note that a linear response argument does not uniquely identify the magnitude of an elementary charge. (One encounters examples where frustration expresses itself through the presence of charges that are unambiguously "quantized," e.g., when topological constraints are present, or when charge frustration is quite literally due to the presence of electric charge, as in Sec. III below.)

Stillinger’s original method[4] divides up each polar head and hydrophobic tail into monomers, and assigns a unit of charge to each monomer. Suppose for simplicity that \( n_H = n_T \). Then, putting \( \beta = 1/k_B T \), the unit charge is given by

\[
q = \left( \frac{3}{4\pi \beta \rho \Delta^{(2)} n^2} \right)^{1/2},
\]

where \( \rho \) is the number density of amphiphiles. This assignment leads to a Debye length

\[
\lambda = \left( \frac{n \Delta^{(2)}}{6} \right)^{1/2} \propto n^{3/2}.
\]

This result is obviously unphysical, since it violates stoichiometry on length scales that can be as large as many surfactant molecule lengths. This contradiction has gone unnoticed in some subsequent work[5].

It is easy to understand why Stillinger’s assignment leads to incorrect results for long surfactant chains. The repulsion of equally charged monomers on a surfactant head (or tail) leads to the unphysical "swelling" of the molecule. This is avoided by lumping the charges into a single unit per head (tail) of surfactant molecule. This alternative procedure, first introduced by Wu, Chandler, and Smit[6], leads to a Debye length that scales linearly with the number of monomers in a surfactant molecule, which is the correct result. A convenient representation of charge frustration of the Ising model ensues: additional site variables, \( t_i = 0, 1 \), are introduced to tag a fraction of the spins. To each tagged spin \( t_i = 1 \) one assigns a charge,
which is positive if the spin is up, and negative if the spin is down. The charge frustrated Ising Hamiltonian can thus be written as

$$H = -\sum_{ij} J_{ij} s_i s_j - h \sum_i s_i + Q^2 \sum_{ij} \frac{s_i t_i s_j t_j}{r_i - r_j} + \mu \sum_i t_i,$$

(11)

with the correct value of the charge being

$$Q = \left( \frac{3}{4\pi \beta \rho \Delta^{(2)}} \right)^{1/2}.$$

(12)

The number of tagged spins, i.e., the density of amphiphiles \( \rho \), is controlled by the chemical potential \( \mu \).

Tracing out the variables \( \{t_i\} \) leads to a reduced spin 1/2 Hamiltonian, whose statistical mechanics has been studied in detail elsewhere\[1\]. Figure 1 is an indication of the agreement between the measured structure factor and calculations based on the charge frustrated model. Our previous work has shown that the reduced spin 1/2 Hamiltonian, while able to predict the structure of microemulsions with remarkable accuracy, cannot accurately predict their phase diagram; more specifically, it does not predict three-phase coexistence. This deficiency is not at all surprising, since tracing out the variables \( \{t_i\} \) amounts to averaging over the density of surfactant molecules.

To remedy this shortcoming, it is convenient to perform, on each site, the change of variables

$$s = \xi + \eta(1 - \xi^2); \quad t = 1 - \xi^2$$

(13)

where the new variable \( \xi = 0, \pm 1 \) describes density fluctuations in the ternary mixture, and \( \eta = \pm 1 \) describes charge fluctuations. Effecting this transformation yields the Hamiltonian of a charge-frustrated spin 1 Ising model. There are two main advantages of this transformation over the procedure followed in Ref.\[1\]. First, surfactant density fluctuations are decoupled from charge fluctuations, allowing the latter to be integrated out easily, at the Gaussian (Debye-Huckel) level. Second, a proper treatment can be given of hydrogen bonding effects, which cause the water-head interaction to be different from the oil-tail interaction, and are principally responsible for the characteristic shape of the three-phase coexistence region in the phase diagram of oil-water-amphiphile ternary mixture\[7\].
3 Charge frustration in metal-ammonia solutions

Alkali metals dissolve readily in liquid ammonia, and the resulting solution has been known for over a century to possess remarkable electronic and optical properties\[10\]. They can all be traced to the favorable solvation energy of an alkali ion, which is larger in magnitude than the ionization energy of an alkali atom. Thus, metal-ammonia solutions consist of unbound electrons immersed in a sea of ammonia molecules and solvated alkali ions. As the metal concentration rises from zero, these solutions are observed to behave at first essentially as insulators (except for ionic conductivity), until a concentration is reached, where the larger electric conductivity signals the onset of extended electronic states. This behavior can be interpreted as a delocalization effect. However, there are reasons to suspect that the conducting phase possesses a nontrivial structure, as is hinted to by the recent quantum molecular dynamics simulations of Ref. \[11\]. The arguments presented below point to charge frustration and to the resulting possibility of microphase separation in this system.

Ammonia is an electron-rich molecule. The Pauli principle implies that an electron immersed in ammonia feels a strongly repulsive potential when it resides on or near an ammonia molecule. Let us neglect for the moment the existence of the Coulomb interaction, i.e., let us turn off the charge of the electrons. Then, the only way that electrons can mix with ammonia is by taking advantage of density fluctuations in the liquid, which generate small empty cavities, in which an electron may be localized. Cavities that are large enough to host electrons, without excessive cost in zero point energy, are rare. Thus, at a finite electron concentration, confinement becomes unfavorable, and the electronic states become extended. A competing process can take place, however, when the Fermi level reaches the difference in chemical potential between liquid vapor (see Fig. 2). Since the cost of adding electrons in the vapor is essentially zero, the system phase separates into two coexisting phases: electrons in liquid ammonia and electrons in vapor. One can schematically regard the system as an ideal fermion gas, phase separated from liquid ammonia. The interfacial tension is given by the surface tension of ammonia plus a contribution from the inhomogeneous electronic density near the surface of the liquid. Phase separation of ideal fermions from a
sea of classical "blockers" has been observed in the computer simulations of Alavi and Frenkel [12].

The picture described above neglects the Coulomb interaction between electrons and the solvated alkali ions. As we discussed in the previous section, oppositely charged densities cannot phase separate over macroscopic length scales. Phase separation must therefore be charge frustrated, and we may expect that some of the conclusions we arrived at in our study of microemulsions hold true for metal-ammonia solutions as well. Note that in this system charge frustration is not an entropic effect; it is brought about by the interaction potential. The parameters involved are thus unambiguously identified. An interesting new feature is the quantum mechanical nature of one of the components. While a quantitative treatment of this additional feature is left for future work, we outline here the qualitative behavior of the system.

We note that metal ammonia solutions should be isomorphic to binary (water-amphiphile) mixtures, ammonia playing the role of water and the electron and solvated ion densities playing the role of surfactant tail and head densities, respectively. One must identify the basic energy and length scales of this problem. We have mentioned already interfacial tension and width of the "bare" (charge-free) system, whose role is completely analogous to that played in the binary mixture counterpart.

We expect that an additional length scale will be important, which characterizes the range of the frustrating interaction. To estimate it, let us consider an interface in the liquid. The appropriate energy diagram, shown in Fig. 3, is obtained from Fig. 2, with the addition of the Coulomb interaction. We see that the Coulomb interaction allows for the presence of electronic bound states near the surface of the liquid. The energy gained from filling up those states will compete with the bare liquid vapor interfacial tension, to produce a low tension interface, which can become extensive.

We expect electron-ammonia bicontinuity to result as a consequence. This expectation is reinforced by the observation that the frustrating length scale, i.e., the length over which the system restores charge neutrality, should be comparable to the length over which the electron bound states extend outside the surface of the liquid. Given the large dielectric constant of liquid ammonia, this length will be well in excess of a Bohr radius; in fact, it could be several times larger than the surface width of the surface of the liquid. A precise estimate involves computation based on density functional
theory, which we leave for future work. Based on our work on amphiphilic systems, however, we predict that a screening length of order ten Bohr radii will be sufficient for bicontinuity to produce observable effects in the small angle structure factor of metal-ammonia solutions. Indeed, this length corresponds to the mean square length of short polyglycol ether surfactants. Unfortunately, at present, experimental information on the long wave length structure of these solutions is not available to us.

4 Conclusion

Frustration of phase separation by a long range attractive interaction (such as the Coulomb potential) has spectacular consequences on the structure and phase diagram of many physical systems. We have discussed in detail amphiphilic mixtures (which include diblock copolymers as an interesting limit) and metal-ammonia solutions. A simple unifying description of such diverse systems is provided by charge frustrated Ising models, such as the spin 1 model defined by the Hamiltonian (11).

Because Ising models are employed in so many and so diverse areas of physics, one could speculate that other frustrated physical systems exist, which can be described by charge-frustrated Ising models, and, thus, exhibit the rich structural and phase behavior we have discussed in the previous sections. For example, will the presence of vacancies in magnetic systems cause (micro)phase separation? The question of phase separation has been raised recently in relation to the behavior of cuprate superconductors [13], such as La$_{2-x}$Sr$_x$CuO$_4$. The undoped material is an antiferromagnetic insulator, while a high enough concentration of vacancies (typically, a few percent) destroys antiferromagnetic order, and produces a poorly conducting metal, which becomes superconducting at low temperature. Semiclassical expansions of the two dimensional $t - J$ model [14] have produced evidence for phase separation of the vacancies from the spins in these materials. Vacancies, however, carry charge, which gives rise to long range repulsion. This repulsion, which is ignored in the $t - J$ model, would prevent macroscopic phase separation, but could lead to microphase separation.

The example above illustrates an interesting novel feature of charge frustration, namely, that frustration is induced by the presence of charges of the same sign. In the language of charged fluids, one deals here with one compo-
nent plasmas, rather than with the neutral Coulomb gas we encountered in Sec. II. Nevertheless, screening can be expected again to play an important role, by bringing about a second length scale in addition to the short (nearest neighbor) range of the exchange interactions.

Finally, we mention the possibility that a similar one-component plasma mapping might be established, following the work of Kivelson et al., between charge-frustrated models and models of structural glasses and supercooled liquids[15]. The details of this mapping, as well as the origin and magnitude of the additional length scales or of the elementary “charges,” remain to be discovered.

I am indebted to David Chandler and Hyung-June Woo for many stimulating discussions. This work was supported by the National Science Foundation under grant CHE 9508336 and by the Office of Naval Research under grant N00014-92-J-1361.

References

[1] H.-J. Woo, C. Carraro, and D. Chandler, Phys. Rev. E 52, 6497 (1995).
[2] H.-J. Woo, C. Carraro, and D. Chandler, Phys. Rev. E 53, R41 (1996).
[3] K.-V. Schubert and R. Strey, J. Chem. Phys. 95, 8532 (1991); K.-V. Schubert, R. Strey, S. R. Kline, and E. W Kaler, J. Chem. Phys. 101, 5343 (1994); M, Kahlweit, R. Strey, and B. Busse, Phys. Rev. E 47, 4197 (1993).
[4] F. H. Stillinger, J. Chem. Phys. 78, 4654 (1983).
[5] M. W. Deem and D. Chandler, Phys. Rev. E 49, 4268 (1994).
[6] D. Wu, D. Chandler, and B. Smit, J. Phys. Chem. 96, 4077 (1992).
[7] G. Gompper and M. Schick, Self-Assembling Amphiphilic Systems (Academic Press, San Diego, 1994).
[8] M. Kotlarchyk, S.-H. Chen, J. S. Huang, and M. W. Kim, Phys. Rev. Lett. 53, 941 (1984).
[9] M. Teubner and R. Strey, J. Chem. Phys. 87, 3195 (1987).
[10] W. Weil, Ann. Physik 121, 606 (1864); C. A. Seely, J. Franklin Inst. 61, 110 (1871).

[11] Z. Deng, G. J. Martyna, and M. L. Klein, Phys. Rev. Lett. 71, 267 (1993).

[12] A. Alavi and D. Frenkel, J. Chem. Phys. 97, 9249 (1992).

[13] V. J. Emery and S. A. Kivelson, Physica C 209, 597 (1993).

[14] A. Angelucci and S. Sorella, Phys. Rev. B 47, 8858 (1993).

[15] D. Kivelson et al., Physica A 219, 27 (1995).
FIGURE CAPTIONS

1: Small angle structure factor of AOT–D₂O–n-decane mixtures, at varying volume fraction \( f \). (a) \( f = 0.181 \); (b) \( f = 0.237 \); (c) \( f = 0.323 \). The symbols represent the experimental data from [8]. The solid lines are the results of calculations based on the charge frustrated model. We have expanded the inverse long wave length structure factor in powers of the momentum transfer, and truncated the expansion at the fourth order, to make connection with the Teubner-Strey formula [9].

2: Energy level diagram for ideal fermions in a liquid. Fermions with energy below \( E_c \) are localized in cavities inside the liquid. The chemical potential difference between vapor and liquid, \( \mu_v - \mu_l \), represents the energy cost of forming an infinite cavity in the liquid.

3: Energy level diagram for electrons in metal-ammonia solution. This diagram is obtained from Fig. 2 by “switching on” the charges of the electrons and of the solvated ions. Note the discrete Coulomb-like spectrum of electronic states near the surface of the liquid. The electronic states inside the liquid are different from Fig. 2, due to the strong polar nature of the solvent.