Research programme

Purpose and aims

The aim of this research is to identify important molecular mechanisms in complex fluid systems of academic as well as industrial importance. Still, this is fundamental research, and we do not expect to develop any products of commercial relevance. The value of constructing approximate models and theories, is not limited to convenient analytical expressions, or a reduced computational cost. Being forced to make approximations is an excellent route to a deeper understanding of the most important physics. Hence, the development of approximate treatments will still be a vital ingredient of our research. The programme comprises four major sub-projects, and a number of developing initiatives.

1 Lower Critical Solution Temperature Mixtures

1.1 State of the art

Many binary mixtures display a Lower Critical Solution Temperature, LCST. At temperatures below this value, the system is *supra-critical*, i.e. the components are completely miscible. LCST behaviour is more a rule than an exception in polymer solutions.¹⁻³ An important example is poly(ethylene oxide) - water (PEO-water), which has an LCST close to 100°C, for very long polymers. We have developed a model for such mixtures^{4,5} that borrows ideas from Karlström,¹ for bulk solutions. Our approach, based on *classical* statistical-mechanical density functional theory (DFT), is also applicable to heterogeneous environments, i.e. in the presence of particles, pores etc. An LCST is predicted without any (explicit) temperature-dependent interactions. Monomers are assumed to be in either of two classes of states, labelled A and B, where B is more solvophobic than **A**. The degeneracy of the **B** class exceeds that of \mathbf{A} , i.e. the population of solvophobic monomers increases with temperature. This can lead to an LCST.

1.2 Project, significance and preliminary results

1.2.1 Fluid-fluid phase transition at bulk supra-critical conditions

Phase diagrams of fluids will generally be affected by the presence of bounding surfaces, such as in porous environments; so-called capillar $ies.^{6-8}$ One major mechanism for this is the effective truncation of long-ranged, usually attractive, intermolecular interactions, via the inevitable exclusion of fluid by the surfaces. For single-component fluids, which always display an upper critical temperature (UCT) in the bulk, this truncation weakens the overall cohesive energy of the fluid. Hence, the fluid in the capillary can be approximately mapped onto a bulk fluid at a higher temperature. Phase transitions in the capillary can thus only occur at temperatures where the bulk can also display the corresponding transition. That is, the confined fluid will have a *lower* critical temperature than the UCT of the bulk.⁷

In mixtures, matters may become more complex, particularly if they display a bulk LCST. We have demonstrated that pore confinement can cause a significant downward shift of the LCST for a polymer solution in a capillary.⁴ That is, while the bulk is *supra-critical* (does not phase separate) the confined solution may be in a 2-phase region. The responsible mechanism is actually the same as that which makes such a state of affairs impossible in single component fluids: surface truncation makes the confined solution behave as if the temperature were higher. While for a single-component fluid (with a UCT) this allows the bulk to be phase-separated while the capillary is in a supercritical state, the opposite can occur in solutions with an LCST.

This phenomenon may prove to be quite useful in applications involving adsorption from mixtures into porous particles. We have recently,⁹ demonstrated that capillary-induced phase separation (CIPS),⁸ may occur below the bulk LCST, also for mixtures only containing *simple* fluid particles (i.e., without polymers).

Experimental verifications.

We believe it likely that the qualitative nature of the findings presented here, are largely universal. Nevertheless, experimental verification is highly desirable. We are currently using NMR methods to obtain a phase diagram of water-poly(isopropylacrylamide) mixtures in porous environments. We have initiated studies on a system with densely packed, small hydrophobized silica particles, where the "pores" constitute the volume between the beads. We also intend to investigate hydrophobized microporous silica surfaces. As a complementary approach we are considering surface force (AFM/SFA) measurements.

Thin-thick transitions, at a surface.

The work described above indicates that CIPS can occur at temperatures considerably below a bulk LCST, even without specific adsorption of fluid components by pore surfaces (i.e. with only inert surfaces). Similar fluid-fluid transitions may also occur at a single surface, with so-called "thin-thick" (wetting) transitions.

Again, we consider a bulk solution with a demixing regime wherein the solution splits into a concentrated (labelled C), and a dilute (D)phase with respect to one of the components, referred to here as the "solute". Suppose we have such a solution, which is undersaturated (Dphase) adjacent to a single surface (S) which is attractive to the solute species. Above the wetting temperature, T_W , a "thick" film of C phase (with thickness L) may form adjacent to S with a (negative) S-C interfacial tension, γ_{SC} . The price to pay for film formation is a volume contribution, $\Delta f_{CD}L$, due to the lower free energy per unit volume of the D phase, as well as a surface term due to the interface of the C film and the bulk D phase, producing a (positive) surface tension, γ_{CD} . The overall surface free energy cost is given by $\gamma_{thick} = \gamma_{SC} + \gamma_{CD} + \Delta f_{CD}L$. If a thick film does not form there is a small positive adsorption of solvent at the surface, giving the so-called "thin" phase surface free energy, γ_{thin} . At some degree of undersaturation, relative to the bulk dilute phase boundary, we have

 $\gamma_{thick} = \gamma_{thin}$, and the two phases coexist. But



Figure 1: Thin-thick coexistence curves, a for 300-mer polymer solution that displays an LCST. Crosses, plus signs, and circles denote various strengths of a shortranged **B**-specific adsorption potential, with circles denoting the strongest attraction (with a maximum strength of less than 0.4 times the thermal energy, kT). Only the part at, and below, LCST (dashed line) is shown in the latter case, where the lower critical surface temperature is about 8 % below the LCST. For PEO/water this would correspond to about 30 °C.

what happens in an LCST mixture, below the LCST? Then, a *C*-*D* interface cannot form, since there is no "dilute" phase in the bulk, only a single "fluid" (F) phase. Nevertheless, the mechanisms we discussed above are still at play, i.e. the presence of the surface that truncates the intermolecular interactions,. This will make the fluid near the surface behave as if the temperature was higher, potentially greater than the LCST. Hence, it may still be possible for a C phase to form at the surface. This suggests the fascinating possibility of thin-thick transitions under supra-critical conditions. As far as we are aware, this is a novel theoretical prediction. We are currently performing DFT calculations of our implicit solvent on an A/B monomer mixture, of the type described above, with parameters chosen so that a bulk LCST is established (as well as a UCST). We have indeed established thinthick coexistence under conditions that are well below the LCST. Examples are shown in Figure 1. Fundamentally, thin-thick transitions may take place at an inert surface without preferential adsorption of either solution component, in

a manner similar to what is seen in pores, as described above.^{4,9} However, the fluid will be less prone to display such transitions, compared to CIPS in narrow pores. The latter is promoted by the truncating effect from two surfaces, and CIPS does not generate significant interfacial tensions (assuming extended pores). Hence, we have so far only established thin-thick coexistence for surfaces that are somewhat more attractive to the solvophobic **B** monomers. On the other hand, the specific attraction that is required is short-ranged, and quite weak, so we do not rule out that one might observe this also for non-adsorbing surfaces. In contrast to ordinary pre-wetting, the transitions are bounded from below by a *lower* surface critical temperature, rather than a wetting temperature, in addition to the standard upper bound of an upper surface critical temperature (see Figure 1).

1.2.2 Temperature-dependent, polymerinduced interactions

In relatively recent work, Feng *et al.*¹⁰ reported an interesting re-entrant flocculation of colloidal particles in an aqueous solution containing polymers. The mixtures that did display the reentrant behaviour had one common property: a solvent (water) that becomes poorer for the polymer, as the temperature is increased. In those systems, a condensed colloidal phase, at low temperatures, became dispersed upon increasing the temperature. A further increase in temperature, however, generated a flocculated phase.

It turns out that our LCST polymer model (described earlier) is able to reproduce this non-monotonic behaviour, in a generic model where the colloidal particles are represented as simple inert (thus hydrophobic) hard spheres⁵! We emphasize that this is achieved without any (explicit) temperature-dependent interactions. At low temperatures, **A** type monomers are more populous and depletion interactions dominate the polymer-mediated *potential of mean force (PMF)* between colloidal particles. On the other hand, attractive polymer bridging dominates the PMF at higher temperatures, due to adsorption of the (now abundant) **B**-type

monomers to the hydrophobic particles. Interestingly, the intermediate temperature regime is characterized by a PMF which is *repulsive*. This is a crucial and general theoretical observation^{*}, that we were the first to demonstrate.⁵ Using this model, we showed that interactions between colloidal particles, mediated by neutral non-grafted polymers, generally follow the trend: attraction => repulsion (or vanishing interaction) => attraction as the surface affinity toward monomers proceeds from repulsive to attractive.⁵

Armed with this knowledge we have initiated efforts to construct models for specific experimental systems that can be expected to display this kind of behaviour. To this end, we have synthesized poly(styrene) (PS) particles, with a diameter of about 0.2 μ m, that carry short (45-mers) end-grafted PEO chains. We then add "free" 100 kD (2274-mers) PEO chains, and monitor potential flocculation by confocal microscopy. We anticipate that the free polymer will not adsorb at room temperature, where water is a good solvent. For a high enough polymer concentration, this implies attractive depletion interactions. On the other hand, at elevated temperatures, PEO becomes hydrophobic and the dissolved polymers mediate attractive bridging forces. According to our predictions, there should be an intermediate temperature regime where we observe a homogeneous dispersion, stabilized by repulsive polymer-mediated interactions. This is indeed exactly what we have observed! At room temperature, flocs of particles start to form at a high enough polymer concentration. At temperatures near 45 °C, the flocs redisperse and we obtain a homogeneous sample. However, samples at about 75 °C will again display clusters, and eventually phase separation.

As mentioned above, our LCST model, with a representation of \mathbf{A} and \mathbf{B} state monomers, as well as solvent particles (\mathbf{S}), and their mutual interactions, will capture this qualitative behaviour. Nevertheless, by sacrificing a de-

^{*}Our DFT is *exact* for ideal chains with point-like monomers, which also mediate such interactions.

tailed account of underlying mechanisms, including energy/entropy separation, we can construct an even simpler model, where the average degree of hydrophobicity of the PEO monomers is described via an effective Lennard-Jones (L-J) potential, acting between all monomers. For monomers separated by r it is given by, $\phi(r, T) =$ $4\epsilon(T)\left[\left(\frac{\sigma}{r}\right)^{12}-\left(\frac{\sigma}{r}\right)^9\right]$. Note that ϵ depends on the temperature T. We will still keep the more elaborate \mathbf{A}/\mathbf{B} model in mind, which means that the the L-J potential acting between the monomers, should be regarded as an interaction *free* energy, or PMF. We expect stronger L-J interactions, also relative to (the increasing) thermal energy, kT, at elevated temperatures. Guided by a previously established simulation model for PEO in water at room temperature.¹¹ we have set $\sigma = 2.65$ Å, while the bond length is chosen to reproduce the experimentally measured radius of gyration of 100 kDa PEO in water.

From previous work, we establish (effective) model temperatures that correspond to explicit experimental temperatures. In ref.,³ a temperature-dependent "effective" Flory-Huggins (FH) parameter, $\chi_{eff}(T)$, is introduced, and from Figure 11 the same reference, we can estimate values at various temperatures. By assuming the same temperature scaling of our $\epsilon(T)$ as the FH "energy" mixing parameter $\Delta \epsilon_{mix}(T)$, that underlies these $\chi_{eff}(T)$ values, we arrive at a mapping from $\chi_{eff}(T)$ to our L-J system. We also need to address the interaction between a PEO monomer and the bare PS surface. We have chosen to model this attraction by a shortranged truncated (at 0.5 nm) and shifted harmonic potential, acting on all monomers. The surface potential amplitude, Ψ , to reproduce the experimental observation of a repulsion at 45 ⁰C. The optimized amplitude of the PS interaction, Ψ_{ref} , then turns out to give a maximum depth of about kT, at this temperature. In Figure 2, we see that Ψ_{ref} is actually fine-tuned, i.e. even small deviations will lead to strong attractions.

Now we are ready to make theoretical predictions for PMFs and concomitant structures, at higher and lower temperatures, with 45 °C as our reference. Calculated polymer-mediated PMFs,



Figure 2: Responses to the particle-particle PMF (W) to variations of the surface amplitude factor, relative to the reference value, Ψ_{ref} . Ψ_{ref} generates a repulsion at our model representation of 45 °C, which is why it amounts to our optimised choice.

at our model representation of 20 °C, 45 °C, and 75 °C, are collected in Figure 3. The temperature response is quite remarkable, given that the relative difference in absolute temperature (293K - 348K) is modest! This clearly captures



Figure 3: DFT predictions of particle-particle PMFs, at three different temperatures. The bulk concentration of dissolved 2274-mers (100 kDa PEO) is at the experimental value of 6 g/l. The surface density of PS-grafted chains is 0.355/nm² (experimental value).

the experimentally observed non-monotonic stability of the studied dispersions^{*}. Separate simulations utilizing this particle-particle PMF have

^{*}Double-layer and dispersion interactions are in these systems, quite weak compared to polymer-induced forces.

confirmed cluster formation at experimental concentrations, for the two attractive cases.

Using our established model, we can of course also predict PMFs between our grafted particles, in the *absence* of any added polymer. The polymer-induced interactions will then only be due to the tethered chains. According to experiments, clusters will form in samples free of added polymers at 78 °C, but this is close to the "transition point", i.e. they will not form at temperatures substantially lower than this threshold value. It is obviously of interest to see what our theoretical model predicts, at similar temperatures. It turns out (not shown) that our model predicts a pure repulsion at 73 °C, and a strong attraction at 78 °C, in perfect agreement with experimental findings, without any adjustments of the already established theoretical model!

This is only a preliminary first study, where we start with a qualitative theoretical prediction, conduct verifying experiments, the results from which are used to create a *specific* model, based on a minimal set of parameters. We expect this combined theoretical/experimental approach to be useful for a range of other LCST systems, where we emphasize the option to tune interactions by changing the temperature.

2 Dynamic phases

2.1 State of the art

Colloidal dispersions can organize into an array of non-trivial structures under non-equilibrium conditions.¹² This may lead to *dynamic* phase transitions.¹³ There have been several experimental studies of the behaviour of charged colloidal particles in alternating external (AC) fields. For instance, Vissers *et al.* obtained "band"¹⁴ as well as "laned"¹⁵ structures (see illustrations below), in the presence of an applied AC field in 3-dimensional (3D) systems.

2.2 Project, significance and preliminary results

In a recent ACS Nano publication,¹⁶ we presented a 3D simulation study of the dynamic behavior of a (model) colloidal suspension containing charged particles, under the influence of an AC field. We obtained jammed bands perpendicular to the field direction at intermediate frequencies, and lanes parallel with the field at low frequencies. The phase diagram in this system depends upon several variables, including field strength and frequency, as well as particle charge. The main results are summarized in



Figure 4: Representative configurational snapshots of colloidal particles with $\pm 40e$ under applied AC fields, with $E_0 = 0.115 \text{ V}/\mu\text{m}$ and different ω values: (a) 500 Hz, (b) 200 Hz, (c) 10 Hz. Positive particles are displayed as green, whereas negative particles are white. The field direction is indicated by a double-headed arrow.

Graphs (d) and (e) show approximate phase diagrams, including contour plots of the order parameter Ψ is the average of ψ_i , where $\psi_i = \frac{(N_l - N_o)^2}{(N_l + N_o)^2}$. Here, N_l and N_o is the number of neighboring particles of "like" and "opposite" charge, to a selected particle i. $\Psi \approx 0$ corresponds to a completely homogeneous state, but for ordered structures, with separated regions in which the particles mainly have the same charge, Ψ approaches a value of 1. Graph (d) is obtained at a constant maximum field strength $E_0 = 0.115 \text{ V}/\mu\text{m}$, whereas the parameters in graph (e) is constrained by a constant maximum external force $F_0 = E_0q = 0.552 \text{ pN}$.

Figure 4. Jammed structures, with bands perpendicular to the field, are formed at $\omega = 400$ Hz, where we observe a re-entrant behavior. If the absolute charge of the particles is lower than about 20*e*, the force is insufficient over an oscillation period of τ_0 to bring about a dynamical instability, and the system remains homogeneous. At absolute charges above approximately 35e, the high charge-charge repulsion between particles is able to inhibit the formation of ordered domains. For intermediate charges, the field is able to create band structures which remain stable across the field period.

The pathway for generating jammed bands is a step-wise mechanism. Firstly, thin bands are obtained, which then penetrate and merge to generate the thicker bands. The formation of laned structures also occurs via intermediate jammed states in some systems. The tendency to form jammed bands is larger under lower frequency, in the regime below 50 Hz. This is due to faster diffusion along the field direction, as well as stronger collisions between adjacent bands. The pressure tensor variations, induced by the collisions between the particles, as well as the changes of work and energy dissipation, are main factors underlying these phase transitions, according to our analyses.

The technical approaches and results shown here provide us with suitable tools for future studies. In this sub-project, we plan to investigate effects of particle polarizability, as well as field-induced anisotropic distributions of the small ions that surround the particles. We also envisage that, particularly for polarizable particles, the *shape* of the particles is important. We expect that our future work in this area will highlight various ways to generate and control these dynamic phases.

3 Many-body interactions

3.1 State of the art

Numerous studies have been devoted to the way in which polymers mediate interactions between colloidal particles. A common approach is then to utilize polymer-induced pair interactions, to investigate (say) colloidal stability and phase behaviours. However, this is not an adequate strategy for cases where the polymers are of similar size to, or larger than, the particles - the so-called "protein limit". Many-body particleparticle interactions are then important, i.e. the interaction between two particles is influenced by the presence of other particles.

We have developed an analytical theory for the many-body PMF between N spherical particles immersed in a continuum polymer fluid.^{17,18} The theory is almost exact for a Θ polymer solution in the "protein limit", i.e. with small particles and long polymers. Note that this also defines the very circumstances under which *N*body effects are important. Importantly, the many-body PMF that is utilized in the MC simulations only requires *summations over particle pairs*. Hence, these simulations are no more demanding than if the particles interact via a standard pair potential. The computational saving compared to an explicit polymer model, can of course be enormous. Numerous evaluations^{17,18} have demonstrated that the many-body theory is remarkably accurate.

Our previous work on systems containing nonadsorbing particles, from simulations as well as mean-field calculations, show that many-body interactions have a *profound* effect on phase diagrams, leading to exceedingly dilute coexisting particle phases, as the average polymer length increases. This causes the coexistence region to



Figure 5: Phase diagrams, for a system containing a θ solvent, polydisperse polymers, and non-adsorbing particles of radius R_S . The length unit is set by the monomer-monomer bond. The particle volume fraction is given by η . The monomer concentration is fixed, with $4\pi\Phi_p R_G^2 = 0.2$, where Φ_p is the reservoir polymer density. Mean-field predictions that result if higher order interactions (beyond pair) are ignored, are shown as a reference.

close up and form a cusp at the percolation transition. This is in stark contrast to the often used pair approximation, where only 2-body forces are considered to act, as illustrated in Figure 5.

3.2 Project, significance and preliminary results

We have recently¹⁹ verified the many-body prediction of a "closed" phase diagram (Figure 5), by performing grand canonical simulations of spherical + non-adsorbing rod-like particles. These simulations were complemented by a simple mean-field theory, to further justify our numerical predictions. The qualitative nature of the phase diagram, for this rods + sphere mixture, as well as a simulation snapshot of a demixing system, are provided in Figure 6. We ar-



Figure 6: A schematic description of the simulated phase diagram, for mixtures of spherical non-adsorbing particles, and polymerizing rod-like polymers. The rods do not need to be polymerizing, but conditions are chosen such that the monomer concentration (that builds up the rod-like chains) is constant.

gue that mixtures of particles and rod-like polymers also would be a feasible *experimental* system, which we predict will display this kind of behaviour. This is because the intra-molecular correlations are not screened in a good solvent for rod-like polymers, as they are with flexible polymers. The length of the rods can grow and become the dominant length scale that determines the range of the depletion interactions for the embedded non-adsorbing particles.

These are just a few demonstrations on the importance of many-body interactions, and the usefulness of our approximate many-body theories, which provide new benchmarks in this field. We have only begun to explore these systems, and we have recently initiated a number of other

interesting systems, where many-body interactions are prominent. An example is a binary mixture model for gels, wherein small particles adsorb the polymers, whereas large ones do not (work in progress). Another interesting class of system, is colloidal dispersions at low ionic strength, whereby the Debye screening length may exceed the size of the particles. This will generate many-body interactions. Finally, we shall devote extra attention to critical Casimir interactions, as detailed below.

3.2.1 Critical Casimir forces

Fisher and deGennes²⁰ predicted that the range of the PMF between two colloidal particles is determined by the solution correlation length, which diverges at the critical point of the dispersing solution. These so-called critical Casimir forces (CCFs) have indeed been measured in experiments. CCFs are independent of the specific nature of the dispersing solution, and display universal behavior subject only to the boundary conditions of the confining particle surfaces.

We are developing a many-body potential of mean force for adsorbing particles, immersed in a critical fluid. We use both mean-field and the Fisk-Widom²¹ version of DFT to show that many-body effects have a profound influence on critical Casimir interactions. Space limitations do not admit a full exposure of our approach but we try to highlight the basic strategy.

We consider a system of N identical spherical particles held in a fixed configuration within a sub-volume V embedded in a bulk near critical fluid. The bulk fluid is at the critical density ρ_c and at a temperature $T \gtrsim T_c$, where T_c is the critical temperature. The particles are identical hard spheres with radius R_S , and they adsorb fluid particles. To describe the fluid in the field of the fixed particles we will use a square gradient approximation to the free energy, ω . Expanding the excess free energy in terms of the excess density, $\tilde{\rho}(\mathbf{r}) = \rho(\mathbf{r}) - \rho_c$, gives

$$\beta \Delta \omega = \frac{D}{2} \int |\nabla \tilde{\rho}(\mathbf{r})|^2 d\mathbf{r} + \omega_{surf} + (1)$$
$$\frac{a}{2} \int \tilde{\rho}(\mathbf{r})^2 d\mathbf{r} + \frac{b}{\delta + 1} \int \tilde{\rho}^{(\delta + 1)} d\mathbf{r}$$

where the surface adsorption term is given by $\omega_{surf} = -\sum_{i=1}^{N} \int_{S_i} \tilde{\rho}(i; \mathbf{s}) \epsilon_0 d\mathbf{s}$, with $\tilde{\rho}(i; \mathbf{s})$ denoting the surface density at particle *i*, whereas ϵ_0 measures the adsorption strength. *D* is a positive constant,²² and, following Marconi,²³ $b = (\partial^3 \mu / \partial \rho^3)_T / 6$ and $a = a_0 [(T - T_c) / T_c]^{\gamma}$ (μ is the chemical potential).

There are two main options for the exponents. With $\delta = 3$ and $\gamma = 1$ we arrive at the classical (Landau) functional whereas $\delta = 5$ and $\gamma = 4/3$ gives a rational²³ version of the phenomenological Widom-Fisk model. Minimizing the functional wrt $\tilde{\rho}$ we get:

$$\nabla^2 \tilde{\rho}(\mathbf{r}) - \lambda^2 \tilde{\rho}(\mathbf{r}) - \eta \tilde{\rho}^\delta(\mathbf{r}) = 0 \qquad (2)$$

where $\lambda^2 = a/D$, and $\eta = bD$. At the surfaces, the gradient is related to the adsorption strength:

$$D\nabla\tilde{\rho}(i;\mathbf{s})\hat{\mathbf{n}}(\mathbf{s}) = -\epsilon_0 \tag{3}$$

where $\hat{\mathbf{n}}$ is a normal vector at the surface of sphere *i*. From these relations, we arrive at an expression for the equilibrium free energy, ω_{eq} :

$$\beta \omega_{eq}(\mathbf{R}) = -\frac{1}{2} \sum_{i=1}^{N} \int_{S_i} \tilde{\rho}(i; \mathbf{s}) \epsilon_o d\mathbf{s} + \frac{b(1-\delta)}{2(1+\delta)} \int \tilde{\rho}(\mathbf{r})^{(\delta+1)} d\mathbf{r}$$
(4)

Our strategy is to solve the full differential equation numerically, within a "proximal" regime, $R_S < r < R_C$, where R_C is chosen large enough to admit a neglect of the $\eta \tilde{\rho}^{\delta}(\mathbf{r})$ term, for r > 1 R_C . The equilibrium density in the outer region can then be solved analytically, to within a constant. This constant is then established by a match of the density, and its gradient, at R_C . In order to proceed, with treatments of multiple-particle systems, we will utilize a similar approach as we have done for polymeric systems,^{17,18} including the "spherical approximation", according to which the density within the promixal regions are assumed to be spherically symmetric around each sphere. This will allow us to express a many-body PMF, for our N-body system, that only require a sum over particle pairs. The latter will depend on a distance vector, which is conveniently stored in a tabulated

form (but a 1-D functional fit to an analytic expression is also possible). This will allow us to run computationally cheap simulations of manybody effects, under the influence of long-ranged critical density fluctuations.

4 Ionic fluids at electrodes

4.1 State of the art

Recent decades have seen a tremendous development in the field of room temperature ionic liquids, ILs. This is largely driven by their special properties, such as a low vapour pressure, and a high charge density. The latter means that ILs offer advantages as electrolytes in electrochemical processes. The structural properties of ILs and their mixtures in the bulk phase and at interfaces are of course crucial to their performance.

Coarse-grained models are commonly used to address more generic behaviours of ILs, and IL+solvent mixtures. Some of the simplest possible approaches of this kind, employ the socalled restricted primitive model, RPM. Here, the solvent (if any) is treated as a dielectric continuum, while all the ions are hard spheres, with diameter d, each carrying a charge, embedded at the centre. Steric "mismatch" is one of the reasons why many ILs have a low melting temperature. This will not be addressed here. Another reason is an anisotropic charge distribution, in at least one of the components forming the salt. Hence, in order to form a stable liquid under ambient conditions, the RPM needs to be suitably modified to reflect this asymmetry. In this spirit, we introduced an asymmetric restricted primitive model, ARPM,²⁴ as an extension of the RPM (similar models have also been suggested by Patey and co-workers,^{25,26} albeit for charged Lennard-Jones representations). Specifically, all ions carry a hard sphere, with a common hardsphere diameter d.

Recently, we utilized classical DFT to explore the properties of a model, that closely resembles the ARPM. Instead of shifting the central charge location in all ions, we retained an RPM-like central charge for the anions, while the cationic charge was displaced a distance b from the hardsphere centre. This model was denoted the Generalized Asymmetric RPM, (GARPM). In common with the ARPM, the GARPM will only introduce one additional parameter, to the original RPM. Furthermore, a large displacement b will lower the melting point of the bulk fluid - a general property shared with the ARPM. However, the propensity of the GARPM to form ion pairs is considerably lower than the ARPM. One could argue that the GARPM has a somewhat closer resemblance to typical ILs, since these commonly are composed of a roughly spherical anion, and an oligometric cation. Using isobaric bulk simulations, we established a value of b that generates a *liquid* phase with a density typical to ILs, under ambient conditions. We have scrutinized electrochemical properties of the resulting model, where a conducting electrode was immersed in the IL fluid. We then utilized our previously $developed^{27,28}$ classical DFT that is able to (approximately) deal with both ion-ion correlations, and surface polarization using a screened image charge approach.

Interestingly enough, the DFT predicts a possible structural phase transition at the electrode interface, in these systems. The cations are strongly attracted because of their ability to allow their charge to be closer to the electrode surface, placing them close to the dielectric interface. This leads to a strong self-image interaction. On the other hand, the anions are attracted by the overall positive electrode charge. There is then a competition at the surface between a range of positive voltages, where the two phases are structurally quite different. The surface charge density is also different between the two phases, at the same applied potential. This is shown in Figure 7. Note that the differential capacitance becomes very large in the vicinity of a phase transition, displaying a formal divergence, due to a discontinuous change of the surface charge density. A disadvantage of capacitors, compared to batteries, is the fact that the voltage changes during discharge. However, the above findings implies the possibility for a narrow voltage regime, over which the capacitance (and thus energy storing capacity) is very high.



Figure 7: The graph displays she variation of a Legendre-transformed grand potential, with applied voltage, for the GARPM system. The system displays a phase separation, and the red arrow marks the point at which the two phases (A and B) coexist. B is the stable phase below $\Psi_S^{(c)}$, whereas A is the equilibrium phase for higher potentials (see ref.²⁹ for details).

4.2 Project, significance and preliminary results

We recently developed a new, and highly efficient, method to simulate ionic fluids confined by two charged and perfectly conducting surfaces. "Confined" should be interpreted with care, since our grand canonical method ensures that the fluid is in chemical equilibrium with a bulk solution, at some prescribed chemical potential. Using wide surface separations, our system will accurately approximate the behaviours at a single electrode surface. We have recently used this technique to simulate capacitors, with titrating peptides, adsorbed onto the electrode surfaces.³⁰

An important advantage is that we are also able to model a porous electrode, by utilizing a short surface separation. Capillary effects are believed to greatly influence the differential capacitance of supercapacitors, but this has been notoriously difficult to study by simulation models, due to a high computational cost, related to multiple image reflections. In our approach, electrostatic interactions are treated using a modified 3D Ewald sum, which accounts for all image charges (with an infinite number of image reflections) across the conductors, as well as the 2D periodicity, parallel to the macroscopic surfaces. The energy expression is in principle exact, and the method is trivial to implement using existing Ewald codes. We furthermore invoke a Grand Canonical scheme that utilizes a bias potential, which regulates the surface charge density. The applied bias potential also enables us to calculate individual chemical potentials of the ions.

We have initiated a series of simulations that utilizes our new method, in an effort to scrutinize electrode pore size effects in general, and the tantalizing possibility of structural phase transitions (as suggested by our DFT predictions), in particular. We appear to have established such a phase transition, but even within our novel scheme, the simulations are computationally demanding, so we cannot confirm this finding as yet.

We will furthermore utilize the new simulation technique to establish interactions between *conducting* surfaces and particles. Here, we will initially focus on aqueous solutions, and a particularly interesting aspect is a relation (if any) between overcharging at a single surface, and the long-ranged electrostatic surface interaction, in the presence of multivalent ions.

5 Other information

Equipment: NMR, AFM (maybe), SFA(maybe), QCM, ellipsometry, confocal microscope, DLS, processors, compilers.

Infrastructure: N/A

Collaborations: Cliff Woodward, UNSW, Canberra (*projects 1-4*), Daniel Topgaard, LU (1), Istvan Furo, KTH (1). Olle Söderman, LU (1), Sture Nordholm, GU (4), Priyadarshini Thiyam, TU, Berlin (3), Bin Li, Sun-Yat-sen Univ., Zhuhai (2), Yong-Lei Wang SU (2), Ke Ma, TUT, Tijanjin (4), Marie Skepö, LU (1), Martin Trulsson, LU (2).

Other applications: No other application has been submitted to VR.

Independent line of research: N/A

Activity: these sub-projects will require a substantial effort, which is why I will devote 80 % of my work (during 4 years), plus a full PhD project to the fulfilment of these tasks.

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