White Rose Research Online

eprints@whiterose.ac.uk
https://eprints.whiterose.ac.uk
Universities of Leeds, Sheffield and York

Deposited via The University of Leeds.

White Rose Research Online URL for this paper:
https://eprints.whiterose.ac.uk/id/eprint/148317/

Version: Accepted Version

Article:
Ettelaie, R, Murray, BS and Liu, S (2019) On the Origin of Seemingly Non-Surface Active Particles Partitioning between Phase Separated Solutions of Incompatible Non-Adsorbing Polymers and Their Adsorption at the Phase Boundary. Langmuir: the ACS journal of surfaces and colloids, 35 (29). pp. 9493-9503. ISSN: 0743-7463

https://doi.org/10.1021/acs.langmuir.9b00892

Reuse
Items deposited in White Rose Research Online are protected by copyright, with all rights reserved unless indicated otherwise. They may be downloaded and/or printed for private study, or other acts as permitted by national copyright laws. The publisher or other rights holders may allow further reproduction and re-use of the full text version. This is indicated by the licence information on the White Rose Research Online record for the item.

Takedown
If you consider content in White Rose Research Online to be in breach of UK law, please notify us by emailing eprints@whiterose.ac.uk including the URL of the record and the reason for the withdrawal request.

UNIVERSITY OF LEEDS
University of Sheffield
UNIVERSITY of York

On the Origin of Seemingly Non-Surface Active Particles Partitioning between Phase Separated Solutions of Incompatible Non-Adsorbing Polymers and Their Adsorption at the Phase Boundary

Rammile Ettelaie,[†*] Brent S. Murray,[†] and Shujie Liu[†§]

† *Food Colloids & Bioprocessing Group, School of Food Science and Nutrition, University of Leeds, Woodhouse Lane, Leeds, LS2 9JT, UK*

§ *School of Food Science and Biotechnology, Zhejiang GongShang University, Hangzhou, Zhejiang, 310018, China*

Keywords: Water-water interfaces, Phase separated solutions, Particle fractionation, Depletion zone, Bijels

* Corresponding author: Rammile Ettelaie, Tel +44 113343 2981, Fax: +44 113343 2982,

e-mail: r.ettelaie@leeds.ac.uk

ABSTRACT

We have computed the free energy per unit area (i.e., interfacial tension) between a solid surface and two co-existing polymer solutions, where there is no specific interaction between the particles and either polymer, via self-consistent field calculations. Several different systems have been studied, including those where the two polymers differ in molecular weight (M_w) by a factor of ~ 2, or where the polymers have the same M_w but one set of chains is branched with the other linear. In the absence of any enthalpic contribution resulting from adsorption on the solid particle surface, the differences in free energy per unit area resulting from the polymer depleted regions around the particles in the two co-exiting phases are found to be ~ 1 $\mu N\ m^{-1}$. Although this value may seem rather small, this difference is more than capable of inducing the partitioning of particles of 100 nm in size (or larger) into the phase with the lower interfacial free energy at the solid surface. By examining the density profile variation of the polymers close to the surface, we can also infer information about the wettability and contact angle (θ) of solid particles at the interface between the two co-existing phases. This leads to the conclusion that for all systems of this type, when the incompatibility between the two polymers is sufficiently large, θ will be close to 90°.

INTRODUCTION

Water-in-water emulsions (W/W) have recently received a great deal of attention from both academic researchers, due to interesting challenges they pose in understanding of their behaviour, and from industrialists attempting to explore their potential in new formulations, particularly in pharmaceutical, agrochemical and food related products.[1, 2, 3, 4] Typically these systems are formed from an aqueous solution of one type of polymer mixed with a solution of another polymer incompatible with the first.[3] Dickinson[4] has recently reviewed the origins of biopolymer phase separation in the context of the stabilization of such dispersions. With both the dispersed phase and the dispersion medium largely consisting of water, an initial significant difficulty in realising these systems is the availability of a suitable surface active stabilising agent. It is obvious that traditional polymeric stabilisers or low M_w surfactants used to formulate O/W or W/O emulsions will simply do not work here. However, it is well established that fine particles also have the ability to act as emulsion stabilisers, leading to the formation of so called Pickering emulsions[5, 6, 7, 8, 9, 10] or even Pickering stabilised gas bubbles.[11, 12, 13, 14, 15, 16] It has been shown experimentally that a similar particle stabilisation mechanism is also possible for W/W type emulsions, as reviewed by Dickinson[4], and in the work conducted by various workers.[1, 3, 17, 18, 19, 20, 21, 22, 23, 24, 25] Aqueous droplets (domains) of one phase are stabilised by adsorption of particles to the W-W interface during the process of nucleation and growth of the domains as the mixed polymer solution undergoes phase separation.

A system closely related to this structure is commonly referred to as a bijel, consisting of interpenetrating continuous domains of one solution within the other. [4, 26, 27, 28, 29, 30, 31, 32, 33] Bijels result from arrested phase separation when the separation proceeds by spinodal decomposition. Once again, it is the presence of particles at the interface and subsequent difficulty in removing them from the interface that provides the required stability of the structure.[4, 26, 29]

Various types of stabilizing 'particles' have been employed for W/W emulsions and bijels[4], ranging from materials with ill-defined surfaces, such as microgel[34] particles and various biopolymer aggregates[19], through to oil droplets[3, 35, 36], polymer lattices[17, 27, 37, 38] and high modulus crystalline or amorphous materials, inorganic[18, 20, 29, 39, 40] or organic[21, 23, 41] and even microbial cells.[1, 30] A large challenge still remains in terms of finding suitable 'biocompatible' particles for use in foods, personal care and pharmaceuticals.[3, 4, 5, 6, 10, 15]

Another motivation for introducing small particles into a slowly phase separating polymer solution is the opportunity that this presents for measuring the microrheology at the scale of the individual growing domains.[42, 43, 44, 45, 46] This is possible by monitoring the Brownian motion of the particles situated within the different domains, using confocal or other suitable microscopy techniques. By measuring the mean square displacement of the particles via suitable image processing techniques, it is possible to extract the viscosity and other relevant rheological parameters for domains of each phase.[4] However, to obtain accurate data, it is vital that any specific interactions between the particle and polymer chains in the system are minimized.[4, 42, 43] Thus, for example, particles with hydrophobic surfaces are often used when the macromolecules in question are strongly hydrophilic. This prevents any adsorption of polymers onto the surface of the particle, greatly reducing the complications that such a process will introduce in interpretation of the measured data. Any adsorption of particles to the interface of the phase-separating domains obviously frustrates extraction of information on viscoelasticity of the interiors of the microdomains.

Most of the interest in particles in W/W emulsions has so far been confined to their surface adsorption properties. Yet the presence of small particles in such systems exhibits other interesting features that also merit study and an explanation. For example, it has been reported in a number of studies that any excess (i.e., non-adsorbed) particles almost exclusively end up residing in one phase but not the other.[3] Furthermore, no matter how the particles are introduced into the system, it is always the same phase that the particles strongly prefer to migrate to.[20, 27, 34, 38, 40] This fact alone suggests that the process is driven by thermodynamic equilibrium considerations, rather than any non-equilibrium slow kinetics. Clearly, when specific interactions favouring one polymer type over the other are at play it is easy to understand why such strong fractionation of particles between the two phases occurs. For example, if one of the polymers in the mix has some degree of affinity for adsorption to the particle surface then, not surprisingly, the particles may well prefer to enter the phase richer in this polymer. This has been discussed in the review by Dickinson[4] and will reduce the maximum interfacial coverage by the particles, i.e., increase the minimum possible domain size in bijels, if this is the factor controlling the arrest of microdomain growth. Yet, it is also thought that this is beneficial in the formation of W/W emulsions in enhancing the ability of particles to stabilise the droplets.[24] Although in many microrheological studies great care is exercised to avoid specific interactions between the particles and all the polymer

species present in the mixture, as mentioned above, strong fractionation of particles continues to be observed.[3, 25] It is the aim of present work to understand this phenomenon.

We consider the simplest possible case involving two incompatible electrically uncharged polymers, both completely neutral with respect to their interactions with the particles, placed in an otherwise theta solvent for both sets of chains. Thus, all interactions are set to zero, apart from the necessary one between the two macromolecules to cause the separation of the system into two separate co-existing solutions. We then examine the partitioning of the particles between these two co-existing phases, which leads us to general conclusions about the preference of such 'neutral' particles for each phase or the W/W interface.

We start first by describing the model and the detail of the calculations in the next section.

MODEL AND METHHODOLOGY

Consider a mixed solution of two incompatible polymers, referred to as polymers 1 and 2 from now on, with overall volume fractions of Θ_1 and Θ_2, respectively. For simplicity the polymers are considered as electrically uncharged, with a short ranged interaction characterised by the Flory-Huggins parameter χ between the monomers of type 1 and 2. The solvent is assumed neutral (i.e., an athermal solvent) for both sets of polymers. As χ is increased, eventually the mixed solution becomes unstable and separates into two distinct solutions[47] α and β, with a compositions (ϕ_1^α , ϕ_2^α) for α and (ϕ_1^β , ϕ_2^β) for solution β. The total amount of polymer for each species is conserved in the system, thus leading to

$$\nu\phi_i^\alpha + (1-\nu)\phi_i^\beta = \Theta_i \quad , \qquad (1)$$

where ν denotes the volume fraction of phase α , and i=1 or 2. In order to determine (ϕ_1^α , ϕ_2^α) and (ϕ_1^β , ϕ_2^β), as well as ν, we note that the chemical potentials of both sets of polymers and solvent molecules have to be equal in both phases, when at equilibrium; $\mu_1^\alpha = \mu_1^\beta$, $\mu_2^\alpha = \mu_2^\beta$ and $\mu_0^\alpha = \mu_0^\beta$, where suffix i=0 refers to solvent.[48, 49] The chemical potential of each polymer specie in a tertiary solution of composition (ϕ_1 , ϕ_2) is quite generally given as[50]

$$\mu_1 = f\left(\phi_1,\phi_2\right) - \phi_2 \frac{\partial f}{\partial \phi_2} + \left(1-\phi_1\right)\frac{\partial f}{\partial \phi_1}$$

$$\mu_2 = f\left(\phi_1,\phi_2\right) - \phi_1 \frac{\partial f}{\partial \phi_1} + \left(1-\phi_2\right)\frac{\partial f}{\partial \phi_2} \quad , \qquad (2)$$

and that for solvent as

$$\mu_0 = f\left(\phi_1,\phi_2\right) - \phi_1 \frac{\partial f}{\partial \phi_1} - \phi_2 \frac{\partial f}{\partial \phi_2} \quad . \qquad (3)$$

In equations 2 and 3, the function *f* represents the free energy density of mixing (i.e., free energy of mixing per unit volume) evaluated at any given mix ratio. Various sophisticated expressions for $f(\phi_1,\phi_2)$ exist in the literature, but these often tend to be for specific types of mixtures. For the purpose of current study it suffices to take a simple but more general mean-field model, such as the expression for *f* provided by Flory-Huggins theory; $f = (\phi_1 / N_1)\ln\left(\phi_1\right) + (\phi_2 / N_2)\ln\left(\phi_2\right) - \left(1-\phi_1-\phi_2\right)\ln\left(1-\phi_1-\phi_2\right) + \chi\phi_1\phi_2$, where N_1 and N_2 are the degrees of polymerisation of polymer 1 and polymer 2 and in general are not equal to each other. Eqs 1, 2 and 3, considered for all the components, yield five non-linear equation which need to be solved simultaneously to determine the values of five variables ϕ_1^{α}, ϕ_2^{α}, ϕ_1^{β}, ϕ_2^{β} and ν. The equations can be solved numerically using multi-dimensional Newton-Raphson method or alternatively, as was done here, by publicly available MINPACK library, first published by Argonne National Laboratory, for solving a set of simultaneous non-linear equations. The latter itself is based on a modification of the so called Powell's method, the details of which can be found in many text books on numerical methods.[51] It is helpful in this respect to first use eq 1 to substitute for ϕ_1^{β} and ϕ_2^{β} in terms of other unknown variables, in eqs 2 and 3. This reduces the number of equations to three which are then more conveniently solved for the three remaining variables, ϕ_1^{α}, ϕ_2^{α} and ν.

With the composition of the two co-existing phases determined, we next compute the free energy change that the introduction of a solid surface (i.e., that of the particle) in each of the two solutions entails. This task is most conveniently achieved using the self-consistent field (*SCF*) calculations, widely used in the study of polymeric systems to investigate both

their interfacial[52, 53, 54, 55] as well as the bulk behaviour.[56, 57, 58, 59] As mentioned before, we consider the simplest but also in many ways the most interesting case, where both sets of polymers have no specific interactions or affinity for adsorption onto the solid surface. This situation can almost be realised in practice, for example by choosing two incompatible water soluble polysaccharides as the polymers, and by making the surface of the particles sufficiently hydrophobic. At distances far from the solid interface, the density profiles of the polymers in the solution will be uniform and as specified by the composition of the phase under consideration. Closer to the surface the profiles will start to vary with distance from the wall, purely due to size exclusion effects. The purpose of the *SCF* calculations is to obtain the density profile variation of each polymer such that together the free energy of the system is minimised. This most probable set of profiles is assumed to completely dominate and thus determine all the thermodynamic properties of the system The details of the theory and its implementation can be found in many excellent books,[60, 61] reviews[62] and other reported work in the literature.[54, 63, 64] Therefore, here we restrict ourselves to providing only a brief overview.

The Scheme used in implementing the *SCF* calculations is that originally proposed by Scheutjens and Fleer.[61, 63, 64] In this scheme, the bulk of the solution next to the solid interface is divided into a set of layers of thickness a_o each. Layers are all parallel to the surface and situated at increasingly further distances away from the solid wall, starting from the first layer adjacent to it. The composition of the solution within each thin layer is assumed to be uniform and equal to the mean value in that layer. However, the volume fraction of the polymers can vary from one layer to next, as one moves further away from the interface. In principle one can use any chosen value for the layer thickness a_o. However, in the Scheutjens and Fleer method the value of a_o is taken to be the nominal size of the monomers comprising our polymer chains[61, 63, 64]. This is also assumed to be the size of the solvent molecules. In doing so, this discretised scheme, ultimately required in any numerical solution to *SCF*, acquires a physical interpretation and essentially becomes identical to the lattice model for polymers in solution.

Numerical calculation of the most probable profile involves an iterative procedure in which the composition of each layer is systematically altered in turn in such a way as to

reduce the free energy of the system. Convergence is obtained when the free energy functional is no longer reduced by altering the composition of the system in any of the layers. The free energy functional is not only dependent explicitly on the volume fractions of the polymers and solvent in every layer, $\phi_i(r)$ (where i=1, 2 and 0), but also implicitly on these through a set of auxiliary fields,[52, 65] $\psi_i(r)$. At the point of convergence these field acquire values

$$\psi_i(r) = \psi_h(r) + \sum_{j \neq i} \chi_{ij} \left(\phi_j(r) - \Theta_j \right) \quad . \quad (4)$$

The first term on the right hand side of the equation is simply a hard core potential acting equally on all monomers, as well as the solvent molecules in a given layer, irrespective of their type. It insures the incompressibility of the solution in each and every layer r, namely that

$$\sum_i \phi_i(r) = \sum_i \Theta_i = 1 \quad . \quad (5)$$

The second term in the potential in eq. (4) is the field that a monomer of type i, residing in layer r will experience due to its interactions with the surrounding monomers. To be more precise, this potential is measured with reference to the environment that the monomer would experience if it was placed well away from the wall. Thus, far from the interface, where all $\phi_i(r)$'s take on their respective bulk values for the given phase (i.e. Θ_i) the value of the fields is zero, as is expected. We also recall that in the problem of interest here, all χ_{ij} are set to zero, apart from χ_{12} which characterises the degree of incompatibility between monomers belonging to polymer type 1 with those of polymer type 2. The *SCF* calculations are initiated by choosing a set of guess solutions for the fields $\psi_i(r)$'s in each layer. The volume fraction $\phi_i(r)$'s resulting from the influence of these fields are then evaluated with the aid of the so called segment density distribution functions. The details of these and efficient numerical methods to compute them can once again be found in many excellent reviews and references and therefore will not be reproduced here.[61, 66] With the volume fraction profiles $\phi_i(r)$ now available, a new set of fields $\psi_i(r)$ can be recalculated from (4) and used to revaluate $\phi_i(r)$. This process is then repeated until the fields and the volume fraction profiles "self consistently" lead to each other, with no significant further changes detected from one iteration to the next. The volume fraction profiles are now the ones that can be shown to minimise the free energy. Furthermore, the value of the free energy at this point is the

interfacial energy resulting from introduction of a solid surface into the solution, thus also being the central quantity of interest to the present study.

In the next section we shall apply the above procedure to several different phase separating polymer solutions to calculate the difference in the solid-solution interfacial energy between the two co-existing phases. The systems studied will include those involving two incompatible linear polymers, at equal overall concentrations, but having different sizes. We also consider the situation where the chains have equal size and concentrations, but one of the polymers is highly branched while the other remains linear. Finally, the case where polymers of equal size and similar architecture, but having different overall concentrations will be considered too.

RESULTS AND DISCUSSION

Case of unequal sized polymers. We begin by first considering a solution consisting of equal volume fractions of our two incompatible polymers. Experiments involving the formation of W/W emulsions are conducted at polymer concentrations typically between 2 to 7% by w/w. For commonly used polysaccharide biopolymers in such experiments,[3, 47] these values translate roughly to volume fractions in the range 1.5 to 5%. Therefore, in this section we fix the overall volume fraction of each type of polymer in the solution at 5%, while we consider the behaviour of the system as the degree of incompatibility between two sets of chains is progressively increased. The sizes of the two polymers are unequal, but both are relatively large linear chains at 500 monomers for polymer 1, and 1200 monomers for polymer 2.

At low values of χ the solution remains homogenous. Once the value of χ is above 0.026 (k_BT) the solution separates into two distinct phases. The composition of each phase is calculated according to the procedure outlined in the previous section and the results are displayed in Figure 1. The solid curves show the volume fractions in phase A, whilst the dotted lines are for phase B. Likewise, the black lines refer to polymer 1 whereas the grey ones represent the volume fractions for polymer 2. Initially the composition of the two phases is similar at the point of entry into the two phase region (i.e. $\chi \sim 0.026$), with most of the system consisting of phase A. However, as the two types of polymer are made more

incompatible, different chains become increasingly segregated. Eventually, for sufficiently large values of χ, phase A consists almost entirely of polymer 1 and phase B only of polymer 2. At this stage the volume fractions of the phases also become the same. All these results are very much as one may expect.

Using *SCF* calculations we can now compute the density profiles of the polymers close to a solid surface, as well as the resulting free energy change per unit area (i.e. interfacial tension) that the introduction of such a solid particle surface into the solution entails, for each of the two distinct phases. The results for the latter set of quantities are presented in Figure 2, showing interfacial tensions (energies) plotted as a function of incompatibility parameter χ. Once again the solid line is for phase A and the dotted one for phase B. The variation of the volume fraction of the polymers, with distance away from the surface, are displayed as solid lines in Figure 3a (phase A) and Figure 3b (phase B). The results are for a system with χ=0.04 (k_BT) as an example. The existence of depletion regions, partially devoid of polymer chains, are evident in both phases. The depletion arises from the well-known drop in configurational entropy of chains close to the interface, since the macromolecules cannot penetrate the solid surface. Because the chains have no specific affinity for the surface they tend to avoid the interfacial region. It is the free energy changes (increases) associated with these depletions zones that are responsible for the interfacial tensions at the solution-solid interfaces for these non-absorbing polymers.

Interestingly, it can be seen from Figures 3a and 3b, that the extents of the depletion zone in both phases are roughly the same, ~ 1 nm. At low polymer concentrations the thickness of the depleted region is determined by the radius of gyration of the polymers, but at higher levels is known to become independent of this. For these more concentrated solutions it is the concentration dependent mesh (or blob size) that determines the extent of the depletion zone.[50, 67] With the total polymer concentration in both phases roughly the same, and the relatively large size of both chains (i.e., both larger than the mesh size), the equal extent of depletion zones is therefore not surprising. Nonetheless, due to differences in the composition mix of the polymers in these two phases and unequal M_w of polymer 1 and 2, the number of macromolecules excluded from depletion zones are not the same. The slight differences in the value of the interfacial tensions γ_{sA} and γ_{sB}, as seen in Figure 2, is a simple reflection of this fact. By convention from now on unless stated otherwise, we refer to the phase having a higher interfacial tension at the solid surface as B, and the one with a lower value as A.

We now consider a small number of solid spherical particles of radius R introduced in the above phase separated system. The free energy associated with a particle in phase A is $4\pi R^2\gamma_{sA}$ and that for phase B is $4\pi R^2\gamma_{sB}$. Irrespective of how the particles were introduced, once equilibrium has been achieved, the ratio of the number density of particles in phase B to that in phase A is

$$\frac{n_B}{n_A} = \exp\left(\frac{-4\pi R^2\left(\gamma_{sB} - \gamma_{sA}\right)}{k_B T}\right) \quad . \qquad (6)$$

where k_B is the Boltzmann constant and T temperature. Thus, even for a small degree of incompatibility $\chi = 0.03$, that just pushes the mixture into the two phase regime, *SCF* calculations predict a difference $(\gamma_{sB} - \gamma_{sA}) = 0.3$ μN m^{-1} (see Figure 2). This leads to a partition coefficient $n_B/n_A = exp(-229) \approx 0$, for 1 μm sized particles ($R = 0.5$ μm). In obtaining this result we took the nominal monomer size in our *SCF* calculations to be 0.7 nm; a reasonable size for sugar moieties that make up the polysaccharide chains. For larger χ values the effect is even stronger, with calculated difference $(\gamma_{sB} - \gamma_{sA})$ approaching 0.96 μN m^{-1}, when χ=0.1. Therefore, it is clear that all the particles in such a system would end up in phase A. This largely explains the experimental observations[3, 25] that particles partition overwhelmingly into one of the phases but not the other, independent of how they are introduced and despite the precautions taken to ensure that the particle surface is neutral with respect to the adsorption of either polymer. It is worth mentioning that, of course the partition coefficient will be a very strong function of the particle size. For example, for particles of size 50 nm, the partition coefficient is much larger, estimated at $exp(-0.57) = 0.56$. Therefore, it may well be possible to use such phase separated polymer solutions to fractionate particles of different sizes. Indeed, this principle is used to fractionate impure biopolymer extracts.[68] If realised, one major advantage of this method will be the lack of any requirement to displace the polymers from the surface of particles, once the separation of particles according to their size is completed.

So far our discussion has primarily focused on the phase in which the excess particles end up. It is also possible to make a number of comments regarding the behaviour of particles trapped at interfaces between the two phases, using the results presented so far. Indeed it is this property that is often the main experimental motivation for the inclusion of particles in these types of phase separated solutions, being the key driver for the formation of

water-in-water emulsions. For this a knowledge of the value of the interfacial tension at the third boundary, namely (γ_{AB}) is desirable. Although the Self-Consistent-Field scheme of Scheutjens and Fleer has been adopted to liquid-liquid interfaces,[69] this remains a somewhat non-trivial task. Nonetheless, it is still possible to deduce from the results obtained in Figure 2, that the value of ($\gamma_{sB} - \gamma_{sA}$) < γ_{AB}, throughout the range of χ values shown in the graphs. The exact reason for this will become more apparent once we have presented our data in the next section. For now it is worth stating immediately that, the inequality implies that the contact angle θ adopted by the particles at the interface (see inset Figure 2), as given by Young's equation

$$\cos(\theta) = \frac{\left(\gamma_{sB} - \gamma_{sA}\right)}{\gamma_{AB}} \quad , \qquad (7)$$

is finite. Thus, while we do not have the exact value of the adsorption energy of the particles attached to the phase boundary between A and B, we can still conclude that a particle shall be at its lowest energy when present at the A-B interface. Note that in using the above equation we make the tacit assumption that the interfacial regions between all the three phases (A, B and solid) are much thinner than size of the particles. For mix ratios just within the two phase region, the width of A-B interface can become rather broad. This consideration was highlighted in a recent review by Dickinson,[4] but is unlikely to be a significant issue for particles of several hundred nm or larger.

Figure 2 also indicates that the difference between γ_{sA} and γ_{sB} approaches a fixed value ~ 0.96 μN m^{-1}, in the limit of large χ. The values of γ_{sA} and γ_{sB} are dependent on χ for two reasons. Firstly, changing χ alters the composition of phases A and B which in turn effects the number and type of chains excluded from the depletion zone. Secondly, so long as both polymers are present in a given phase, any variation in the strength of interactions between the chains impacts their distribution in the depleted zone. This latter effect is demonstrated in Figure 3, where we have altered the χ value from 0.04 to 0.03. This is done for each of the phases separately, by deliberately keeping its composition the same (as when χ=0.04), but altering χ so as to move the given mix ratio into the stable one phase region. Small alterations in the density profiles of the polymers are evident only very close to the solid surface, as presented by dotted lines in Figures 3a for phase A, and more clearly in Figures 3b for phase B. Both of the above mentioned factors, through which χ influences γ_{sA}

and γ_{sB}, disappear as the two polymers are made increasingly more incompatible. Once χ is large enough, the polymers become almost completely segregated and further increases in χ cease to alter the composition of A and B. Since each phase is also devoid of one or the other polymer, the strength of interactions between chains is also of no further consequence to the behaviour of polymers near the solid surface. Thus, $(\gamma_{sB} - \gamma_{sA})$ reaches a plateau value independent of χ, in this limit. This is an interesting and useful result. We recall that χ was the only model dependent interaction parameter in our calculations, since the two polymer types were both assumed to have no affinity for adsorption onto the surface of the solid. Thus, we discover that the limiting value of $(\gamma_{sB} - \gamma_{sA})$ is also independent of χ.

While the above argument indicates that $(\gamma_{sB} - \gamma_{sA})$ will approach a constant value, the value of γ_{AB} is obviously still affected by χ. This dependence is widely accepted to have a form $\gamma_{AB} = (k_B T / a_o^2) / (\chi / 6)^{1/2}$ (where a_0 is the unit monomer size) for two long immiscible polymer melts, as was first predicted by Helfand and Tagami[70, 71] using an analytical solution to the self-consistent-field theory, obtained in the context of Cahn-Hilliard approximation. Taking the value of monomer size ~ 0.7nm as has been done so far, for $\chi = 0.1$ we have $\gamma_{AB} = 1$ mN m^{-1}. While we are not dealing with polymer melts here, one expects the same kind of dependence for interfacial tension between two polymer solutions, albeit with changes to pre-factors that account for dilution and any expected broadening of the interfacial region between the two phases. The first of these varies as ϕ^2, whereas the thickness of the interface $d_{int} \sim \phi^{-1/2}$. Therefore, the interfacial tension is expected to scale as $\phi^{3/2}$ in the same limit of infinitely long polymer chains.[72] Broseta et al[73] have suggested that a more appropriate theoretical approach when dealing with semi-dilute solutions, requires the system to be considered as a collection of blobs in accord with the scaling theory of polymers.[50] In other words, one replaces the monomer size by blobs of size $\xi \sim a_o \phi^{-3/4}$ (sometimes also referred to as the mesh size) and consider each chain as consisting of N_b blobs where $N_b \sim N\phi^{5/4}$. The chain is ideal on length scales larger than ξ. This also involves a rescaling of the interaction parameter, from χ between two unlike monomers to u between blobs. It turns out that, the concentration dependent parameter $u(\phi)$ sclaes[73, 74] as $\sim \phi^{0.3}$. For a polymer melt of two similarly sized but otherwise incompatible linear chains, the critical value of χ is easily shown[50] to be $2/N$. By the same token, in a semi-dilute solution this is shown to become[73, 74] $u(\phi^c)=(2/N_b^*)$, where ϕ^c is the critical volume fraction, below which no phase separation occurs at any polymer mix ratio, and N_b^* is the number of blobs comprising each

chain at this particular critical value of ϕ. Thus, at any other polymer volume fraction, using the above scaling form for $u(\phi)$, we have

$$u(\phi) = \frac{2}{N_b^*}\left(\frac{\phi}{\phi^c}\right)^{0.3} \tag{8}$$

as was first proposed by Boresta et al[73] and discussed in more detail by Tromp.[74] Once again, in analogy with polymer melt systems[70], the width of the interface is found to be $d_{int} \approx \xi [6u(\phi)]^{-1/2}$ while the interfacial tension between the two phases becomes[73, 74]

$$\gamma_{AB} = \left(\frac{k_B T}{\xi^2}\right)\left(\frac{u(\phi)}{6}\right)^{1/2} \tag{9}$$

We assume that the blobs are space filling, occupying it uniformly. This leads to

$$\xi^3 N_b n_c = \xi^3\left(\frac{N n_c}{\phi^{-5/4}}\right) = \left(\frac{\xi^3}{a_0^3}\right)\phi^{9/4} \approx 1 \tag{10}$$

where the number density of the chains, n_c, is specified by the overall volume fraction of the polymer $(a_o)^3 N n_c = \phi$. Using equations 8-10, the value of γ_{AB} can be calculated provided that the value of the critical polymer volume fraction ϕ^c is known. For a given solution of interest this data is often taken from the experimental results. However, here we wish to estimate γ_{AB} for a series of otherwise similar systems where only the incompatibility parameter χ is varied. Therefore, we first need to relate ϕ^c to χ. We establish this relation by considering equation 8 in the limiting melt case where $\phi \to 1$ and $\xi \approx a_o$. In this limit the value of $u(\phi=1)$ should coincide with χ. This then leads to $\phi^c \approx (N\chi/2)^{-0.65}$, as opposed to the more familiar classical result $\phi^c \approx (N\chi/2)^{-1}$. Using this, together with equations 9 and 10, we find $\gamma_{AB} = \phi^{1.65}(k_B T / a_0^2)\sqrt{(\chi/6)}$, which again is to be compared to the expression obtained on the basis of the classical theory[72, 73] i.e. $\gamma_{AB} = \phi^{1.5}(k_B T / a_0^2)\sqrt{(\chi/6)}$. We substitute the results of our numerical calculations for $\gamma_{sB} - \gamma_{sA}$ (Figure 2), together with the calculated value of γ_{AB} obtained from both the scaling and classical theories, into equation 7 in order to estimate the value of contact angle in each case. Interestingly, for both we find that the contact angle made by an otherwise inert spherical particle at the phase A – phase B interface has $\cos(\theta) \sim \chi^{-1/2}$, for sufficiently large values of χ. This follows from the fact that $(\gamma_{sB} - \gamma_{sA})$ approaches a χ independent constant as $\chi \to \infty$ (Figure 2), whereas $\gamma_{AB} \sim \chi^{1/2}$. That is to say, that for a

sufficiently large degree of incompatibility, $\cos(\theta) \approx 0$, and the contact angle made by an inert solid particle at the A-B phase boundary will approach 90^0. It should be noted that at arriving at this result we have used expressions for γ_{AB} that are, strictly speaking, valid at either high values of χ or long polymers chains $N\chi \rightarrow \infty$. Corrections for cases where $N\chi$ is not sufficiently large were obtained by Boresta et al[73] and later recalculated more accurately by Tromp and Blokhuis.[75] Accordingly to the latter authors, these corrections can be significant and as large as 20% in some realistic scenarios. They arise because of a higher accumulation of solvent at the phase boundary, thus reducing the contacts between the two incompatible polymers at the liquid-liquid interface. Also for finite size polymers the presence of a small amount of each polymer in the phase rich in the other contributes to further corrections. Both of these factors were shown[75] to reduce the actual value of γ_{AB}. In this sense then, the formula $(k_B T / \xi^2) / (u(\phi)/6)^{1/2}$ used here can be taken to represent the upper limit of γ_{AB}.

In the range of χ=0.03 to 0.1 for our system, the value of θ is already found to be very close to 90 ($\theta \approx 88^0$). For example at χ=0.1, the equation derived from the scaling theory gives γ_{AB} = 24.3 μN/m, which in turn gives $\cos(\theta)$ = (0.96/24.3) and a contact angle of $\theta = 87.7^0$. We note that corrections of up to 20% in γ_{AB} will hardly alter the fact that θ remains close 90^0 (For example reducing γ_{AB} by 20% to 19.4 μN/m only changes $\theta = 87.2^0$). We expect this result to hold true for all polymer phase separated systems containing such inert particles, provided the system is sufficiently within the two phase regime and not too close to the binodal line. The estimated value of γ_{AB} from the classical theory predicts a contact angle that is even closer to 90^0. Consequently, the adsorption energy of the particle also becomes ~ $\pi R^2 \gamma_{AB}$. It should be noted that in practice, the work to displace a particle from an interface is several times greater than this value.[76, 77] This is due to the dissipation of the stored energy in the fluid neck, created between the particle and the surface during the displacement of the latter, as the fluid bridge relaxes back once the particle is fully detached and has left the interface. Furthermore, recent work of Keal at al[78] has demonstrated the interesting possibility for the existence of long-lived metastable states and long relaxation kinetics for particles trapped at liquid-liquid interfaces.

Case of polymers with different architectures. Unequal values of the interfacial tension between the co-existing phases and a solid surface, in phase separated polymer solutions, can also arise due to differing architectures of the two incompatible polymers. In this section we repeat the calculations performed in the previous section, but now choose to make the degree of polymerisation the same for both groups of chains. This is set at 901 monomers. Similarly, the volume fraction of both polymers is made equal, at 2%. The only remaining difference between polymer 1 and polymer 2 now is their architectures, continuing to be linear for polymer 2, but polymer 1 having a highly branched dendrimeric type structure as depicted schematically in Figure 4. In this somewhat idealised branched polymer model, the bifurcation occurs at precise intervals of every 20 monomers. Recently we developed an efficient way of incorporating such complex branched structures in the framework of Scheutjens and Fleer *SCF* theory with relative ease.[79] The same technique has been utilised here.

Figure 5 presents the calculated data for the variation of γ_{sA} and γ_{sB} with the incompatibility parameter χ, where phase A is found to consist predominantly of branched and phase B of linear chains. The interfacial tensions are found to be smaller than those in the system considered in the previous section. This is expected and is mainly due to the lower overall polymer concentrations involved. The most striking difference between the results of Figure 5, and the previous ones in Figure 2, is the existence of two separate branches for the upper curve representing γ_{sB}. These are shown as long dashed and short dashed lines in Figure 5. The two branches look as if they would crossover at a value of χ marginally above 0.16. Close to this point, the *SCF* iterations were found not to converge so easily, and when they did they took many more steps to do so. Initially, considering the branch at higher values of χ, this is found to exhibit the same behaviour as that in Figure 2. Once again, as the degree of incompatibility is made larger, so the difference $(\gamma_{sB} - \gamma_{sA})$ increases at first, but then plateaus at ~ 0.9 $\mu N\ m^{-1}$ independent of χ. Note that this plateau value is quite similar in value to that for the two linear polymers of different length in Figure 2. This value also serves as a lower bound for the value of γ_{AB}, as will be discussed later below. Recently, Nicolai and co-workers have managed to measure interfacial tensions lower than 10 $\mu N\ m^{-1}$ for coexisting polymer solution phases. The measurements were performed using a method based on the relaxation of the shape of a droplet.[3, 19] Even lower values (as low as 1 $\mu N\ m^{-1}$) have been suggested, and even measured.[4, 37] While the predicted value

0.9 μN m^{-1} is indeed very small, it is still quite sufficient to cause a higher energy $4\pi R^2 (\gamma_{sB} - \gamma_{sA}) = 700\ k_B T$ (for particles of 1 μm size) when residing in phase B as opposed to phase A. Once again this is more than enough to cause the overwhelming partitioning of particles into phase A (branched polymer rich) at equilibrium and their complete absence in phase B (linear polymer rich).

Next we consider the more unexpected branch of γ_{sB} vs. χ curve (the short dashed line in Figure 5), seen for χ values large enough to lead to phase separation, but $\chi < 0.16$. The rapid change of the plotted quantity with the variation in χ makes it unlikely that this quantity is actually γ_{sB}. To elucidate the nature of the calculated value, it is constructive to examine the density profiles of polymers close to the solid surface, for both of the co-existing phases. Figures 6 displays these data, where the concentration profiles at the interface are superimposed for both phases, making their comparison easier. The profiles are those for a system with $\chi = 0.13$. The solid lines show the results for phase A and the dashed ones for phase B. Similarly, the black lines are for branched polymers and grey ones for linear chains. Both branched and linear polymers, not having any affinity for the solid surface, tend to avoid the surface in both phases. However, highly branched polymers, for the same degree of polymerisation, are more compact objects than their linear counterparts. The larger depletion zone associated with the linear chains allows the accumulation of more compact branched chains at the outer edges of this depletion region. This is reflected as a slight maximum in the concentration of branched chains, seen occurring at a short distance away from the surface (black lines) in Figure 6. More notable is the behaviour observed in phase B (linear chain rich phase) at even larger distances away from the solid interface. It is found that the concentration profiles of both sets of polymers (dashed lines) alter to coincide with those for phase A (solid lines), as one approaches the solid surface. In other words, we now have two interfaces. The first of these is between the solid surface and phase A and the second one, located further away, between phase A and the bulk phase B solution. The interface between phase A and B is rather broad ~ 45 nm, but its position is roughly indicated by the arrow in Figures 6.

An important feature of the *SCF* calculations is that they are designed to converge to polymer density profiles that possess the minimum free energy for the system. Seen as such, the above results can be understood when $\gamma_{AB} + \gamma_{sA} < \gamma_{sB}$. For now it energetically pays to have two interfaces, i.e., solid to A, plus A to B, as opposed to a single interface, solid to B.

Consequently, for χ values where this is true, the *SCF* calculations also converge to concentration profiles that display this behaviour. In the system here this occurs for χ values above the single phase region, but less than 0.16. For $\chi > 0.16$, the opposite is true and $\gamma_{AB} + \gamma_{sA} > \gamma_{sB}$. Incidentally, for $\chi > 0.16$, the *SCF* calculated profiles (not shown here) exhibited no such behaviour as that in Figures 6, and instead were very similar to those found in Figures 3a and 3b. From this discussion it is also obvious that the values calculated, and shown as the short dashed part of the upper curve in Figures 6, are not actually γ_{sB}, but rather $(\gamma_{AB} + \gamma_{sA})$. Thus the difference between the upper and the lower curve (solid line), in this part of the phase diagram, represents the interfacial tension between the two incompatible solutions, γ_{AB}. Given the much stronger dependence of γ_{AB} on χ in comparison with the other two interfaces, it is now also clear why the short dashed curve, representing $(\gamma_{AB} + \gamma_{sA})$, alters so rapidly with increasing level of incompatibility χ. The value of γ_{AB} is seen from Figures 6 to be only around 0.3 $\mu N\ m^{-1}$ for $\chi = 0.14$, but is expected to become significantly larger for higher χ values. Regarding the behaviour of small particles at A-B interfaces at lower values of $\chi < 0.16$, where we have $\gamma_{AB} + \gamma_{sA} < \gamma_{sB}$, the particles will be fully wetted by the branched polymer rich phase, i.e., phase A. Above this value a finite contact angle, viz. Young's equation, eq. 7, exists.

The actual value $\chi = 0.16$ is of course system dependent, being different for polymers of different architecture, concentration or size. But one expects the general result to hold true and that for systems marginally within the two phase regime, the particles to be fully wetted by one of the phases and cease to adsorb onto the interface between this and the other phase. One implication is that this may limit the smallest practically realisable structures in bijel-type systems. Here the structure is stabilised by the presence of particles at the interface between two interpenetrating domain networks. Bijels are often created via spinodal decomposition, where the domains of the two phases are not only initially growing in size, but also evolving in their composition to reach the final values for each respective phase. At the early stages of such phase separation, the compositions of the two incompatible phases are not very different. They are more similar to what we may expect for lower χ, in contrast to their eventual fully evolved values predicted on the basis of the true degree of incompatibility. Thus, it is only later on in the process that the true final compositions begin to manifest themselves and particles would begin to adsorb onto the interface. This delay in adsorption will set a lower limit on the size of stabilised domains achievable in such an

experiment. Whether it is this effect and/or the kinetics of diffusion and adsorption of particles to the interface that is ultimately the more significant limiting factor in stabilising the fine structures of bijel systems, is an interesting question for future theoretical consideration.

Systems with different polymer concentrations. For a pair of incompatible polymers, under given conditions, the value of χ is largely predetermined. While it is possible to alter this parameter by changing the temperature, quality of solvent, etc., controlling the exact value is not so simple. Much easier is to change the concentration of the polymers in any experimental system. For this reason and for the sake of completeness, we also consider the changes in the solid-solution interfacial tensions occurring within our phase separated system as the overall polymer concentration is altered. In order to do so, we return to our original system consisting of two linear incompatible biopolymers, having different degrees of polymerisation 500 and 1200. However, this time we keep the incompatibility parameter χ =0.15. Instead we vary the overall volume fraction of the polymers in the system, while continuing to assume that half of the chains (by volume) belong to polymer 1 and the other half to polymer 2.

The results are summarised in Figure 7. The system remains a homogenous single phase when the volume fraction of each polymer is less than a value marginally below 0.02. For higher volume fractions phase separation into two distinct solutions occurs. The compositions of the two phases continue to diverge from each other as the amount of polymer in the system is increased. By the time we have a concentration of 0.04 for each polymer, phase A consists almost exclusively of the shorter chains and B mainly of the larger polymers. Both γ_{sA} and γ_{sB} increase rapidly with higher polymer concentrations (see inset graph in Figure 7), reaching values of ~ 0.1 mN m^{-1} when volume fraction of each polymer is 0.055 (i.e. a total of 0.11). The difference ($\gamma_{sB} - \gamma_{sA}$) remains much smaller in comparison (Figure 7). Near the binodal line it has a value very close to zero, as expected. However, by the time the overall polymer volume fraction is 0.11, ($\gamma_{sB} - \gamma_{sA}$) is approximately 1.1 μN m^{-1}, a result which again is not too dissimilar to the plateau values we obtained for the systems considered in the previous sections. Thus, once again this difference in the interfacial energy of the two phases with the solid surface is enough to strongly bias the partitioning into phase A of particles a few hundred nm diameter, or larger. We also note that in the range of

polymer concentrations studied (0.02 to 0.11), the polymer density profile variations close to the solid surface indicated no evidence for a distinct phase A-phase B interface, much the same as in Figure 3 and unlike for the branched system in Figure 6. Again, we can take this as the evidence that, at least for this range of polymer concentrations, $\gamma_{AB} + \gamma_{sA} > \gamma_{sB}$ and therefore the solid particle will have a finite contact angle at the boundary between the two co-existing solutions. It is possible that for solutions slightly more dilute than 0.02, but still just concentrated enough to lead to phase separation, the situation will be different. However, it was quite difficult to obtain convergence of *SCF* calculations, when dealing with phase B close to binodal line.

One may also speculate on whether $(\gamma_{sB} - \gamma_{sA})$ may continue to increase, decrease or plateau out at yet even higher concentrations than those shown in Figure 7. From a practical point of view, study of concentrations much higher than 10% involving polysaccharides are very difficult due to very high solution viscosities and extremely slow kinetics. But our calculations provide some evidence that the value of $(\gamma_{sB} - \gamma_{sA})$ in Figure 7 may in fact have a maximum and is likely to decrease at some point for more concentrated solutions, if these were to be realised in practice.

CONCLUSIONS

In this work we have computed the free energy per unit area (i.e., interfacial tension) between a solid surface and each of the two co-existing polymer solutions, where there is no specific interaction between the particles and either polymer. As expected there are polymer depleted regions around the particles in both phases. The differences $(\gamma_{sB} - \gamma_{sA})$ in the interfacial tensions between the two phases and the particle surface are found to be ~ 1 μN m^{-1} for several systems: including polymers differing in molecular weight or architecture. While this absolute value is rather small, for particles of size several hundred nm or larger, this difference is more than capable of enticing the partitioning of the particles towards the phase possessing the lower interfacial free energy with the solid surface.

By examining the density profile of the polymers close to the solid interface we can also identify whether $(\gamma_{sB} - \gamma_{sA}) > \gamma_{AB}$, or vice versa. When $\gamma_{sB} > \gamma_{sA} + \gamma_{AB}$, we detect the formation of two boundaries, one between phase B and phase A and the other between phase A and the solid surface, when the solid is placed in phase B. When $\gamma_{sB} < \gamma_{sA} + \gamma_{AB}$, we predict

that for a large degree of incompatibility (high value of χ) between the two biopolymers, ($\gamma_{sB} - \gamma_{sA}$) approaches a plateau value. As a result, $\cos(\theta) \sim \chi^{-1/2}$, where θ is the contact angle made by the solid particle adsorbed at the A-B interface. In other words $\theta \rightarrow 90^0$ as χ becomes sufficiently large in these type of systems.

It is also worth highlighting that our work has largely focused on the behaviour of a single particle (i.e., a dilute particle system). For systems containing a larger number of particles, the presence of depletion zones can give rise to the well-known phenomenon of depletion attraction between the particles. This can occur in both phases, the particles undergoing depletion flocculation. When particles have some tendency for adsorption at the A-B interface, as discussed above, such aggregates could form and accumulate at these boundaries.[4] This may be useful in aiding stronger stabilisation of water-in-water emulsions or indeed in locking in finer structures required in bijel systems. Certainly further simulation work is required to explore the possibilities of such scenarios.

ACKNOWLEDGEMENTS

The authors wish to thank Eric Dickinson for many fruitful discussions and M. Janny for their suggestion for improving the convergence of our numerical calculations. One of us (RE) also acknowledges Taco Nicolai for his useful comments and in particular for pointing out the possibility of using these types of phase separated solutions in fractionating particles according to their size.

REFERENCES

1. Esquena, J. Water-in-water (W/W) emulsions. *Curr. Opin. Colloid Interface Sci.* **2016,** *25*, 109-119.

2. Frith, W. J. Mixed biopolymer aqueous solutions - phase behaviour and rheology. *Adv. Colloid Interface Sci.* **2010,** *161* (1-2), 48-60.

3. Nicolai, T.; Murray, B. Particle stabilized water in water emulsions. *Food Hydrocolloids* **2017,** *68*, 157-163.

4. Dickinson, E. Particle-based stabilization of water-in-water emulsions containing mixed biopolymers. *Trends Food Sci. Technol.* **2019,** *83*, 31-40.

5. Dickinson, E. Food emulsions and foams: Stabilization by particles. *Curr. Opin. Colloid Interface Sci.* **2010,** *15* (1-2), 40-49.

6. Dickinson, E. Use of nanoparticles and microparticles in the formation and stabilization of food emulsions. *Trends Food Sci. Technol.* **2012,** *24* (1), 4-12.

7. Berton-Carabin, C. C.; Schroen, K. Pickering Emulsions for Food Applications: Background, Trends, and Challenges. In *Annual Review of Food Science and Technology, Vol 6*, Doyle, M. P.; Klaenhammer, T. R., Eds.; Annual Reviews: Palo Alto, 2015; Vol. 6, pp 263-297.

8. Binks, B. P. Colloidal Particles at a Range of Fluid-Fluid Interfaces. *Langmuir* **2017,** *33* (28), 6947-6963.

9. Yang, Y. Q.; Fang, Z. W.; Chen, X.; Zhang, W. W.; Xie, Y. M.; Chen, Y. H.; Liu, Z. G.; Yuan, W. E. An Overview of Pickering Emulsions: Solid-Particle Materials, Classification, Morphology, and Applications. *Front. Pharmacol.* **2017,** *8*, 20.

10. Linke, C.; Drusch, S. Pickering emulsions in foods - opportunities and limitations. *Crit. Rev. Food Sci. Nutr.* **2018,** *58* (12), 1971-1985.

11. Du, Z. P.; Bilbao-Montoya, M. P.; Binks, B. P.; Dickinson, E.; Ettelaie, R.; Murray, B. S. Outstanding stability of particle-stabilized bubbles. *Langmuir* **2003,** *19* (8), 3106-3108.

12. Dickinson, E.; Ettelaie, R.; Kostakis, T.; Murray, B. S. Factors controlling the formation and stability of air bubbles stabilized by partially hydrophobic silica nanoparticles. *Langmuir* **2004,** *20* (20), 8517-8525.

13. Murray, B. S.; Ettelaie, R. Foam stability: proteins and nanoparticles. *Curr. Opin. Colloid Interface Sci.* **2004,** *9* (5), 314-320.

14. Binks, B. P.; Horozov, T. S. Aqueous foams stabilized solely by silica nanoparticles. *Angew. Chem.-Int. Edit.* **2005,** *44* (24), 3722-3725.

15. Murray, B. S. Stabilization of bubbles and foams. *Curr. Opin. Colloid Interface Sci.* **2007,** *12* (4-5), 232-241.

16. Valadbaigi, P.; Ettelaie, R.; Kulak, A. N.; Murray, B. S. Generation of ultra-stable Pickering microbubbles via poly alkylcyanoacrylates. *J. Colloid Interface Sci.* **2019,** *536*, 618-627.

17. Nguyen, B. T.; Nicolai, T.; Benyahia, L. Stabilization of Water-in-Water Emulsions by Addition of Protein Particles. *Langmuir* **2013,** *29* (34), 10658-10664.

18. Vis, M.; Opdam, J.; van 't Oor, I. S. J.; Soligno, G.; van Roij, R.; Tromp, R. H.; Erne, B. H. Water-in-Water Emulsions Stabilized by Nanoplates. *ACS Macro Lett.* **2015,** *4* (9), 965-968.

19. de Freitas, R. A.; Nicolai, T.; Chassenieux, C.; Benyahia, L. Stabilization of Water-in-Water Emulsions by Polysaccharide-Coated Protein Particles. *Langmuir* **2016,** *32* (5), 1227-1232.

20. Peddireddy, K. R.; Nicolai, T.; Benyahia, L.; Capron, I. Stabilization of Water-in-Water Emulsions by Nanorods. *ACS Macro Lett.* **2016,** *5* (3), 283-286.

21. Chatsisvili, N.; Philipse, A. P.; Loppinet, B.; Tromp, R. H. Colloidal zein particles at water-water interfaces. *Food Hydrocolloids* **2017,** *65*, 17-23.

22. Abbasi, N.; Navi, M.; Tsai, S. S. H. Microfluidic Generation of Particle-Stabilized Water-in-Water Emulsions. *Langmuir* **2018,** *34* (1), 213-218.

23. Ben Ayed, E.; Cochereau, R.; Dechance, C.; Capron, I.; Nicolai, T.; Benyahia, L. Water-In-Water Emulsion Gels Stabilized by Cellulose Nanocrystals. *Langmuir* **2018,** *34* (23), 6887-6893.

24. Gonzalez-Jordan, A.; Nicolai, T.; Benyahia, L. Enhancement of the particle stabilization of water-in-water emulsions by modulating the phase preference of the particles. *J. Colloid Interface Sci.* **2018,** *530*, 505-510.

25. Moschakis, T.; Chantzos, N.; Biliaderis, C. G.; Dickinson, E. Microrheology and microstructure of water-in-water emulsions containing sodium caseinate and locust bean gum. *Food Funct.* **2018,** *9* (5), 2840-2852.

26. Cates, M. E.; Clegg, P. S. Bijels: a new class of soft materials. *Soft Matter* **2008,** *4* (11), 2132-2138.

27. Firoozmand, H.; Murray, B. S.; Dickinson, E. Interfacial Structuring in a Phase-Separating Mixed Biopolymer Solution Containing Colloidal Particles. *Langmuir* **2009,** *25* (3), 1300-1305.

28. Lee, M. N.; Thijssen, J. H. J.; Witt, J. A.; Clegg, P. S.; Mohraz, A. Making a Robust Interfacial Scaffold: Bijel Rheology and its Link to Processability. *Adv. Funct. Mater.* **2013,** *23* (4), 417-423.

29. Cai, D. Y.; Clegg, P. S. Stabilizing bijels using a mixture of fumed silica nanoparticles. *Chem. Commun.* **2015,** *51* (95), 16984-16987.

30. Firoozmand, H.; Rousseau, D. Food-grade bijels based on gelatin-maltodextrin-microbial cell composites. *Food Hydrocolloids* **2015,** *48*, 208-212.

31. Hijnen, N.; Cai, D. Y.; Clegg, P. S. Bijels stabilized using rod-like particles. *Soft Matter* **2015,** *11* (22), 4351-4355.

32. Rumble, K. A.; Thijssen, J. H. J.; Schofield, A. B.; Clegg, P. S. Compressing a spinodal surface at fixed area: bijels in a centrifuge. *Soft Matter* **2016,** *12* (19), 4375-4383.

33. Tao, L.; Ke, C.; Dobnikar, J. Research progress of bicontinuous interfacially jammed emulsion gel (Bijel). *Acta Phys. Sin.* **2018,** *67* (14), 12.

34. Murray, B. S.; Phisarnchananan, N. Whey protein microgel particles as stabilizers of waxy corn starch plus locust bean gum water-in-water emulsions. *Food Hydrocolloids* **2016,** *56*, 161-169.

35. Hanazawa, T.; Murray, B. S. Effect of Oil Droplets and Their Solid/Liquid Composition on the Phase Separation of Protein-Polysaccharide Mixtures. *Langmuir* **2013,** *29* (31), 9841-9848.

36. Hanazawa, T.; Murray, B. S. The influence of oil droplets on the phase separation of proteine-polysaccharide mixtures. *Food Hydrocolloids* **2014,** *34* (1), 128-137.

37. Balakrishnan, G.; Nicolai, T.; Benyahia, L.; Durand, D. Particles Trapped at the Droplet Interface in Water-in-Water Emulsions. *Langmuir* **2012,** *28* (14), 5921-5926.

38. Nguyen, B. T.; Wang, W. K.; Saunders, B. R.; Benyahia, L.; Nicolai, T. pH-Responsive Water-in-Water Pickering Emulsions. *Langmuir* **2015,** *31* (12), 3605-3611.

39. Herzig, E. M.; White, K. A.; Schofield, A. B.; Poon, W. C. K.; Clegg, P. S. Bicontinuous emulsions stabilized solely by colloidal particles. *Nat. Mater.* **2007,** *6* (12), 966-971.

40. Murray, B. S.; Phisarnchananan, N. The effect of nanoparticles on the phase separation of waxy corn starch plus locust bean gum or guar gum. *Food Hydrocolloids* **2014,** *42*, 92-99.

41. Inam, M.; Jones, J. R.; Perez-Madrigal, M. M.; Arno, M. C.; Dove, A. P.; O'Reilly, R. K. Controlling the Size of Two-Dimensional Polymer Platelets for Water-in-Water Emulsifiers. *ACS Central Sci.* **2018,** *4* (1), 63-70.

42. Moschakis, T. Microrheology and particle tracking in food gels and emulsions. *Curr. Opin. Colloid Interface Sci.* **2013,** *18* (4), 311-323.

43. Moschakis, T.; Murray, B. S.; Dickinson, E. Particle tracking using confocal microscopy to probe the microrheology in a phase-separating emulsion containing nonadsorbing polysaccharide. *Langmuir* **2006,** *22* (10), 4710-4719.

44. Cucheval, A. S. B.; Vincent, R. R.; Hemar, Y.; Otter, D.; Williams, M. A. K. Multiple Particle Tracking Investigations of Acid Milk Gels Using Tracer Particles with Designed Surface Chemistries and Comparison with Diffusing Wave Spectroscopy Studies. *Langmuir* **2009,** *25* (19), 11827-11834.

45. Mukhopadhyay, A.; Granick, S. Micro- and nanorheology. *Curr. Opin. Colloid Interface Sci.* **2001,** *6* (5-6), 423-429.

46. Waigh, T. A. Microrheology of complex fluids. *Rep. Prog. Phys.* **2005,** *68* (3), 685-742.

47. Semenova, M.; Dickinson, E. *Biopolymers in food colloids: Thermodynamics and molecular interactions*; Brill: Leiden, 2010.

48. Antipova, A. S.; Semenova, M. G. Effect of neutral carbohydrate structure in the set glucose/sucrose/maltodextrin/dextran on protein surface activity at the air/water interface. *Food Hydrocolloids* **1997,** *11* (1), 71-77.

49. Semenova, M. G.; Antipova, A. S.; Belyakova, L. E.; Misharina, T. A.; Terenina, M. B.; Golovnya, R. V. Influence of maltodextrins with a different dextrose

equivalent on the interaction between hexyl acetate and legumin in an aqueous medium. *Abstr. Pap. Am. Chem. Soc.* **1999,** *218*, U55-U55.

50. de Gennes, P.-G. *Scaling concepts in polymer physics*; Cornell University press: New York, 1979.

51. Press, W. H.; Flannery, B. P.; Teukolsky, S. A.; Vetterling, W. T. *Numerical recipes: The art of scientific computing*; Cambridge University press: Cambridge, 1986.

52. Ettelaie, R.; Dickinson, E.; Pugnaloni, L. First-order phase transition during displacement of amphiphilic biomacromolecules from interfaces by surfactant molecules. *J. Phys.-Condes. Matter* **2014,** *26* (46).

53. Evers, O. A.; Scheutjens, J.; Fleer, G. J. Statistical Thermodynamics of Block Copolymer Adsorption .1. Formulation of the Model and Results for the Adsorbed Layer Structure. *Macromolecules* **1990,** *23* (25), 5221-5233.

54. Leermakers, F. A. M.; Atkinson, P. J.; Dickinson, E.; Horne, D. S. Self-consistent-field modeling of adsorbed beta-casein: Effects of pH and ionic strength on surface coverage and density profile. *J. Colloid Interface Sci.* **1996,** *178* (2), 681-693.

55. Pickett, G. T.; Balazs, A. C. Equilibrium behavior of confined triblock copolymer films. *Macromol. Theory Simul.* **1998,** *7* (2), 249-255.

56. Fredrickson, G. H.; Ganesan, V.; Drolet, F. Field-theoretic computer simulation methods for polymers and complex fluids. *Macromolecules* **2002,** *35* (1), 16-39.

57. Mezzenga, R.; Ruokolainen, J.; Fredrickson, G. H.; Kramer, E. J. High internal phase polymeric emulsions by self-assembly of colloidal systems. *Macromolecules* **2003,** *36* (12), 4466-4471.

58. Shi, A. C.; Noolandi, J. BINARY-MIXTURES OF DIBLOCK COPOLYMERS - PHASE-DIAGRAMS WITH A NEW TWIST. *Macromolecules* **1995,** *28* (9), 3103-3109.

59. Noolandi, J.; Hong, K. M. Effect of block copolymers at a demixed homopolymer interface. *Macromolecules* **1984,** *17* (8), 1531-1537.

60. Grosberg, A. Y.; Khokhlov, A. R. *Statistical Physics of Macromolecules* AIP press: New York, 1994.

61. Fleer, G.; Stuart, M. C.; Leermakers, F. Chapter 1 - Effect of Polymers on the Interaction between Colloidal Particles. In *Fundamentals of Interface and Colloid Science*, Lyklema, J., Ed.; Academic Press, 2005; Vol. 5, pp 1.1-1.94.

62. Lifshitz, I. M.; Grosberg, A. Y.; Khokhlov, A. R. Some problems of the statistical physics of polymer chains with volume interaction. *Reviews of Modern Physics* **1978,** *50* (3), 683-713.

63. Scheutjens, J.; Fleer, G. J. Statistical-theory of the adsorption of interacting chain molecules .1. Partition-function, segment sensity distribution, and adsorption-isotherms. *J. Phys. Chem.* **1979,** *83* (12), 1619-1635.

64. Scheutjens, J.; Fleer, G. J. Stastical -theory of the adsorption of the interacting chain molecules .2. Train, loop, and tail size distribution. *J. Phys. Chem.* **1980,** *84* (2), 178-190.

65. Ettelaie, R.; Khandelwal, N.; Wilkinson, R. Interactions between casein layers adsorbed on hydrophobic surfaces from self consistent field theory: κ-casein versus para-κ-casein. *Food Hydrocolloids* **2014,** *34*, 236-246.

66. Fleer, G. J.; Cohen Stuart, M. A.; Scheutjens, J. M. H. M.; Cosgrove, T.; Vincent, B. *Polymers at interfaces*; Chapman and Hall: London, 1993.

67. Mao, Y.; Cates, M. E.; Lekkerkerker, H. N. W. Depletion force in colloidal systems. *Physica A* **1995,** *222* (1-4), 10-24.

68. Hu, B.; Han, L. Y.; Gao, Z. M.; Zhang, K.; Al-Assaf, S.; Nishinari, K.; Phillips, G. O.; Yang, J. X.; Fang, Y. P. Effects of temperature and solvent condition on phase separation induced molecular fractionation of gum arabic/hyaluronan aqueous mixtures. *Int. J. Biol. Macromol.* **2018,** *116*, 683-690.

69. Lyatskaya, Y.; Gersappe, D.; Gross, N. A.; Balazs, A. C. Designing compatibilizers to reduce interfacial tension in polymer blends. *J. Phys. Chem.* **1996,** *100* (5), 1449-1458.

70. Helfand, E.; Tagami, Y. Theory of interface between immiscable polymers. *Journal of Polymer Science Part B-Polymer Letters* **1971,** *9* (10), 741-&.

71. Helfand, E.; Tagami, Y. Theory of interface between immiscable polymers .2. *J. Chem. Phys.* **1972,** *56* (7), 3592-&.

72. Hong, K. M.; Noolandi, J. Theory of interfacial tension in ternary homopolymer-solvent systems. *Macromolecules* **1981,** *14* (3), 736-742.

73. Broseta, D.; Leibler, L.; Kaddour, L. O.; Strazielle, C. A theoretical and experimental study of interfacial tension of immiscable polymer blends in solution. *J. Chem. Phys.* **1987,** *87* (12), 7248-7256.

74. Tromp, R. H. Water-Water Interfaces. In *Structure and Functional Properties of Colloidal Systems*, 1st ed.; Hidalgo-Alvarez, R., Ed.; CRC Press: Boca Raton, 2017.

75. Tromp, R. H.; Blokhuis, E. M. Tension, Rigidity, and Preferential Curvature of Interfaces between Coexisting Polymer Solutions. *Macromolecules* **2013,** *46* (9), 3639-3647.

76. Ettelaie, R.; Lishchuk, S. V. Detachment force of particles from fluid droplets. *Soft Matter* **2015,** *11* (21), 4251-4265.

77. Lishchuk, S. V.; Ettelaie, R. Detachment Force of Particles with Pinning of Contact Line from Fluid Bubbles/Droplets. *Langmuir* **2016,** *32* (49), 13040-13045.

78. Keal, L.; Colosqui, C. E.; Tromp, R. H.; Monteux, C. Colloidal Particle Adsorption at Water-Water Interfaces with Ultralow Interfacial Tension. *Phys. Rev. Lett.* **2018,** *120* (20), 6.

79. Ettelaie, R.; Holmes, M.; Chen, J. S.; Farshchi, A. Steric stabilising properties of hydrophobically modified starch: Amylose vs. amylopectin. *Food Hydrocolloids* **2016,** *58*, 364-377.

Figure captions

Figure 1. The volume fraction of polymers in each of the two co-existing phase separated solutions, plotted against the degree of incompatibility χ between different polymer species. Degree of polymerisation was 500 for polymer 1 and 1200 for polymer 2.

Figure 2. Variation of the interfacial tension between the solid surface and each of the two co-exiting phases, plotted versus the incompatibility parameter χ. The systems are the same as those considered in Figure 1. The inset shows location of a particle at the interface between the two phases, and demonstrates the contact angle θ, as that measured in phase A.

Figure 3. Variation of the density profile of each polymer in the interfacial region close to the solid surface, shown as solid lines for (a) phase A, rich in smaller chains (i.e. polymer1) (b) phase B, rich in longer chains (i.e. polymer 2), for a system with χ=0.04. The grey lines represent polymer 1 and black ones polymer 2. The dashed lines show the corresponding results obtained at a slightly different χ value of 0.03, but for the same compositions as the two separated solutions obtained when χ was 0.04.

Figure 4. A schematic of the highly branched chain model, indicating the number of branches and branching points, as is used in the present study.

Figure 5. Variation of the interfacial tensions (γ_{sB} and γ_{sA}) of the solid surface with each of the two phase separated solutions, shown as a function of the incompatibility parameter χ. Both sets of polymers have the same degree of polymerisation 901, but with polymer 1 being branched (see Figure 4) and polymer 2 linear. The dashed line is for γ_{sB} and the solid one for γ_{sA}. The upper branch curve seen at lower values of χ, shown here by the short dashed line, is in fact ($\gamma_{sA} + \gamma_{AB}$) and not γ_{sB}, as is discussed in the text.

Figure 6. Density profiles of branched (black) and linear (grey) polymers at the interfacial region close to an inert solid surface, for the system of Figure 5. The solid lines are for A (branched rich) and dashed ones for B (linear rich) phases, respectively. The value of χ was 0.13 here. The arrow indicates the approximate location of an A-B interface, formed some distance away from the surface, for the phase B case.

Figure 7. The difference in the interfacial tension at solid-phase B and solid-phase A, plotted against the overall polymer volume fraction, for the system of Figure 1. The volume fraction of the two polymer is assumed equal and χ=0.15, here. The inset shows the variation of each of γ_{sB} (dashed line) and γ_{sA} (solid line), with the overall volume fraction of each polymer in the system.