INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **14** (2002) L1–L8 PII: S0953-8984(02)28952-3

LETTER TO THE EDITOR

Entropic wetting and the fluid–fluid interface of a model colloid–polymer mixture

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Received 19 September 2001, in final form 22 November 2001
Published 7 December 2001
Online at stacks.iop.org/JPhysCM/14/L1

Abstract
A recent density functional theory is used to investigate the free interface between demixed fluid phases in a model colloid–polymer mixture. Both the colloid and polymer density profiles oscillate on the colloid-rich side of the interface, provided the polymer reservoir packing fraction η_p^r is sufficiently high. Results for the surface tension are in reasonable agreement with experiment. When the mixture is adsorbed against a hard wall, entropic depletion effects give rise to a wetting transition whereby the colloid-rich phase wets completely. Prior to complete wetting we find three layering transitions, the first of which extends far into the single-phase region. This pattern of surface phase transitions is very different from that observed for simple one-component fluids at planar substrates.

Adding non-adsorbing polymer to a colloidal suspension can considerably enrich the bulk phase behaviour. In particular, for sufficiently large size ratios R_g/R_c, where R_g is the radius of gyration of the polymer and R_c is the radius of the colloid, a colloid–polymer mixture can exhibit stable colloidal gas, liquid and solid phases, with the packing fraction of the polymer reservoir η_p^r playing a role equivalent to that of inverse temperature for a simple substance [1]. Colloidal gas–liquid phase separation is induced by the depletion effect, i.e. an effective attraction between the colloids arises from the exclusion of polymer from the depletion zone between colloids [2]. Although much attention has been paid to the bulk phase behaviour and structure, relatively few experimental [3, 4] or theoretical [5–7] studies have been carried out on the *interfacial* properties of such mixtures. One might expect the entropic depletion mechanism to lead to interesting adsorption phenomena and to rich surface phase behaviour. Here we investigate the free interface between the demixed colloid-poor (gas) and colloid-rich (liquid) fluid phases and the adsorption of the mixture at a hard wall using the simple model introduced by Asakura and Oosawa (AO) [2] and Vrij [8], which treats the colloids as hard spheres with radius R_c and the polymer coils as interpenetrating and non-interacting as regards their mutual interactions. The polymer particles are excluded from the

colloids to a centre-of-mass distance $R_c + R_p$, where the polymer 'radius' $R_p = R_g$. Assuming that the polymer is ideal constitutes a drastic oversimplification. Nevertheless the binary AO model does capture the observed variation of the bulk phase behaviour with increasing size ratio $q = R_p/R_c$ [1] and thus it is a natural choice for a first study of inhomogeneous colloid–polymer mixtures. Whilst some progress has been made in calculating the interfacial properties of the AO model, all work to date relies upon a mapping to an effective one-component system of colloids interacting via the AO pairwise potential [5–7]. This approach is useful for certain adsorption situations [6] but does have serious limitations as it is strictly valid only for highly asymmetric mixtures, with $q < 0.1547$, where many-body effective interactions between the colloids are absent [6, 9]. We have recently developed an alternative density functional theory (DFT) for the binary AO model using the techniques of fundamental measure theory (FMT) [10]. Our new functional treats arbitrary size ratios q and is thus able to incorporate the effects of many-body interactions which arise at larger values of q, and which represent an important feature of the model. In bulk a stable (w.r.t. the fluid–solid transition) fluid–fluid demixing transition occurs for $q \geqslant 0.3$ [9]. Our functional accounts for this transition as the bulk free energy is identical to that from the free-volume theory of Lekkerkerker *et al* [11]. The functional yields analytical partial structure factors via the Ornstein–Zernike (OZ) route of a similar quality to those obtained from Percus–Yevick (PY) theory but with the advantage that they are consistent with the bulk free energy, i.e. the thermodynamic and structural routes to the fluid–fluid spinodal are equivalent [10], a property which is especially advantageous for our present studies of interfaces at or near two-phase coexistence. We emphasize that, unlike DFT treatments of interfacial phenomena in simple fluids, where an explicit attractive fluid–fluid potential is treated in a perturbative (mean-field) fashion, here the effective interactions emerge naturally from the DFT and are treated non-perturbatively.

Applying the DFT to the free fluid–fluid interface we find oscillatory behaviour of both the colloid and polymer density profiles on the colloid-rich side for states removed from the bulk critical point. The calculated surface tensions are similar to those measured in real colloid–polymer mixtures [3]. At the hard wall we find novel depletion-induced wetting and layering transitions as the bulk fluid–fluid phase boundary is approached from the colloid-poor side by increasing the colloid packing fraction η_c at fixed η_p^r. At first glance one might expect there to be little difference, in terms of the physical phenomena displayed, between the interfacial properties of this model complex fluid and those of a simple (atomic or molecular) fluid; the colloids behave as an effective one-component fluid where the strength of the attractive interaction is determined by η_p^r. Since for an ideal polymer, and a hard wall, each term in the effective Hamiltonian is proportional to η_p^r [6] one might expect equivalent Boltzmann weights in the two types of fluids. The crucial difference is that the functional now incorporates the effects of two- and higher-body interactions which depend on the distance of the colloids from the wall and which would be present in the effective Hamiltonian for the colloids. Studies of one-component fluids are usually based on a simple pairwise additive potential function for the fluid–fluid interaction and a simple one-body wall–fluid potential representing interactions with a substrate.

Details of the functional are given in [10]. We simply recall that this is constructed using the well-tried recipes of FMT developed for additive hard-sphere mixtures [12]. The full functional is designed to satisfy the zero-dimensional situation of extreme confinement and involves tensor weight functions [10]. Here we employ the simpler version which omits the tensor contribution to the free energy density and which can be regarded as a linearization, in the polymer density, of the original Rosenfeld FMT functional[3]. Density

[3] In equation (6) of [10] we set $\hat{n}^i_{\mathrm{m2}} \equiv 0$.

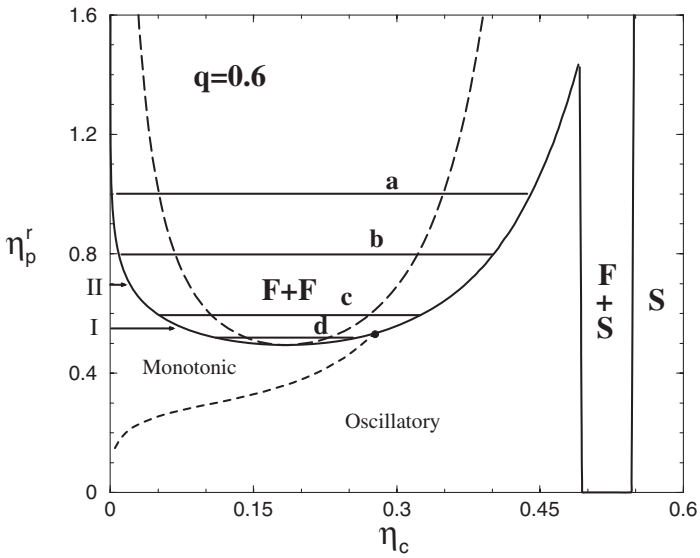

Figure 1. The bulk phase diagram calculated from free-volume theory [9, 11] for $q = 0.6$. η_c is the packing fraction of the colloid and η_p^r that of the polymer in the reservoir. F denotes the fluid and S the solid. The long broken curve shows the fluid–fluid spinodal and the short broken curve shows the (FW) line obtained from DFT (see footnote 4). The latter intersects the binodal at $\eta_{p,\mathrm{FW}}^r = 0.53$. The horizontal tie lines a, b, c, d connect coexisting fluid states. Horizontal arrows indicate paths I and II by which the phase boundary is approached for the adsorption studies of figures 3 and 4.

profiles for colloid (c) *and* polymer (p) are obtained by minimizing the grand potential functional $\Omega[\rho_c(\boldsymbol{r}), \rho_p(\boldsymbol{r})] = \mathcal{F}[\rho_c(\boldsymbol{r}), \rho_p(\boldsymbol{r})] + \sum_{i=c,p} \int \mathrm{d}^3 r (V_i(\boldsymbol{r}) - \mu_i)\rho_i(\boldsymbol{r})$ where $\mathcal{F}$ denotes the intrinsic Helmholtz free energy functional of the AO mixture, μ_i is the chemical potential (fixed by the reservoir) and $V_i(\boldsymbol{r})$ is the external potential coupling to species i with $i = c, p$. In the case of the free interface $V \equiv 0$; for a hard wall $V_c = \infty$ for $z < R_c$ and 0 otherwise, while $V_p = \infty$ for $z < R_p$ and 0 otherwise. z is the coordinate perpendicular to the wall. The thermodynamic state point is specified by the packing fraction of colloids: $\eta_c = 4\pi(R_c)^3\rho_c/3$ and of polymer in the reservoir: $\eta_p^r = 4\pi(R_p)^3\rho_p^r/3$, where ρ_c and ρ_p^r refer to the number densities. Diameters are denoted by $\sigma_c = 2R_c$ and $\sigma_p = 2R_p$.

We consider first the free interface between demixed fluid phases. Figure 1 shows the bulk phase diagram obtained from the present theory for a size ratio $q = 0.6$ for which there is a stable fluid–fluid demixing transition with a critical point at $\eta_{p,\mathrm{crit}}^r \sim 0.495$. It should be emphasized that the fluid–fluid and solid–fluid phase boundaries presented here are those of the original free-volume theory [9, 11]. A full investigation of the freezing properties of the present functional is outside the scope of the present study, which is restricted to fluid states. The colloid density profiles are shown in figure 2. For states approaching the triple point the interfacial width is $\sim\sigma_c$, similar to values inferred from ellipsometric measurements [4]. Striking oscillations develop on the colloid-rich side. The general theory of asymptotic decay of correlations in mixtures with short-range forces predicts that the period and decay length of oscillations in the density profiles of both species should be identical [13]. We confirmed that, for states where the colloid profile oscillates, the corresponding polymer profiles exhibit oscillations, on the same, colloid-rich, side of the interface, with identical period and decay length as those of the colloid.

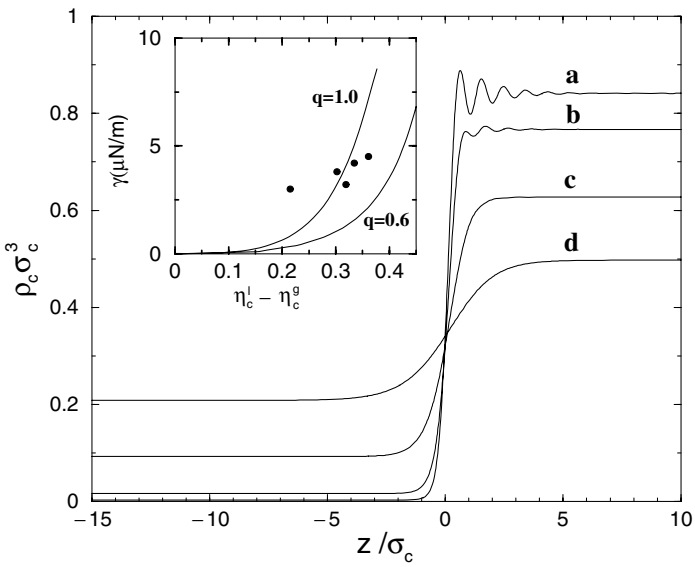

Figure 2. Colloid density profiles for the free interface between demixed fluid phases for a size ratio $q = 0.6$. The polymer reservoir packing fractions correspond to the tie lines in figure 1, i.e. $\eta_p^r = 1.0$ (a), 0.8 (b), 0.6 (c) and 0.52 (d) (near critical point). States a, b and c lie on the oscillatory side of the FW line. The inset shows the surface tension γ versus the difference in the colloidal packing fraction in coexisting liquid (l) and gas (g) phases for $q = 0.6$ and 1.0. The colloid diameter is taken to be 26 nm to compare with experimental data of [3] (points) where $q = 1.0$.

In simple fluids the presence of oscillations in one-body density profiles is intimately connected to the existence of the Fisher–Widom (FW) line which divides the bulk (density–temperature) phase diagram into regions where the asymptotic decay of bulk pairwise correlations is either monotonic or exponentially damped oscillatory [13, 14]. There is an analogous FW line for the present model (see figure 1), where the three partial pair correlation functions change their asymptotic decay simultaneously[4].

For the present mixture oscillatory profiles arise at the free interface when the colloid density in the coexisting liquid is greater than the colloid density where the FW line intersects the binodal, i.e. for all states with $\eta_p^r > \eta_{p,\mathrm{FW}}^r = 0.53$ for $q = 0.6$. However, the amplitude of oscillations can become very small for states just above the FW intersection point and this is why profile (c) does not show oscillations on the scale of figure 2. For state (a) with $\eta_p^r = 1.0$ the amplitude of the oscillations is substantial and appears to be larger than the corresponding amplitude for a square well fluid near its triple point [14]. Thermally induced capillary-wave fluctuations of the interface will act to erode the oscillations in the 'bare' (mean-field) density profiles obtained from DFT. Because of the extremely low surface tensions γ which occur in colloidal systems one might expect the oscillations to be completely washed out by fluctuation effects. However, it is the dimensionless parameter $\omega = k_\mathrm{B}T/4\pi\gamma\xi^2$ which determines the strength of these fluctuation effects and we find that ω takes values of a similar size as those for simple fluids. Further details will be given elsewhere [15]. This is due to the fact that the bulk correlation length ξ scales roughly as σ_c [10] and γ as $1/\sigma_c^2$ [5]. From our explicit calculations of γ and ξ we find that $\omega \approx 0.04$ for states such as (a) in figure 2. This implies

[4] The FW line was determined by calculating the poles of the partial structure factors $S_{ij}(k)$, following [13].

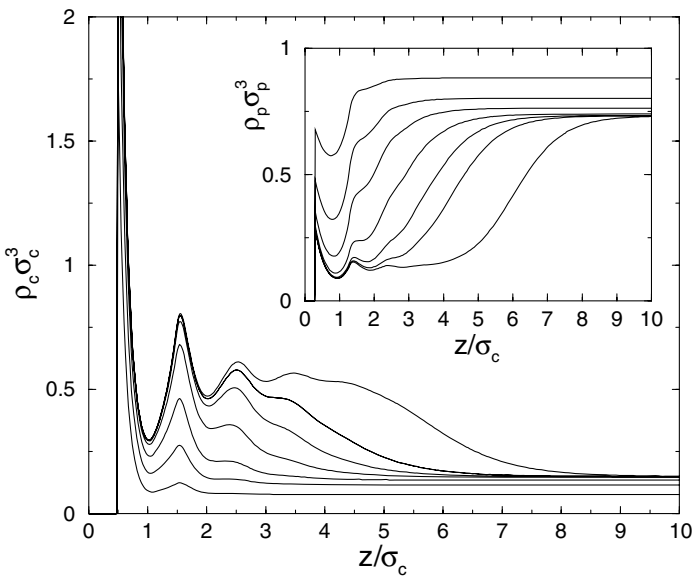

Figure 3. Colloid density profiles showing the complete wetting of a hard wall by the colloid-rich phase at $\eta_p^r = 0.55$ as the bulk phase boundary is approached along path I in figure 1. Bulk colloid fractions are $\eta_c = 0.04$, 0.06, 0.07, 0.076, 0.0775, 0.0778 and 0.0779 (from bottom to top). The inset shows the polymer profiles for the same η_c (from top to bottom).

that detecting oscillations of the colloid profile should be no more difficult than for simple fluids. Indeed, it could be more favourable to investigate such structuring in colloidal systems, where the period is of colloidal size, than in atomic fluids where the period is about one atomic diameter. The inset in figure 2 shows the tension, γ, for size ratios $q = 0.6$ and 1.0. We find that the tension calculated using the present functional is consistently larger than that calculated using the effective one-component Hamiltonian treated by square gradient DFT [5] and agrees better with the experimentally measured tension for mixtures of a silica colloid, coated with 1-octadecanol, and polydimethylsiloxane (PDMS) in cyclohexane at $T = 293$ K [3]. The size ratio for this mixture is approximately 1.0. In order to compare our DFT results with experiment we choose $\sigma_c = 26$ nm, the mean diameter of the particles investigated in [3]; there are no other adjustable parameters in the theory. The measured tensions are 3–4 μN m^{-1}, values which are about 1000 times smaller than tensions of simple fluids. Theory predicts a rapid decrease of the tension as the critical point is approached, i.e. $\gamma \sim (\eta_c^l - \eta_c^g)^3$ in this mean-field treatment. The decrease should be even more rapid for proper Ising-like criticality where the exponent is replaced by $2\nu/\beta \approx 3.9$. That the experimental data do not indicate such a decrease probably reflects the difficulty in working close to the critical point[5].

Next we consider the AO mixture adsorbed at a hard wall. As a test we first calculated profiles for $q = 0.1$ where simulation results are available for the colloid profiles since, for such a small size ratio, the mapping to an effective Hamiltonian with only a pairwise additive fluid–fluid potential and an explicit wall–fluid depletion potential is exact [6]. We find that the present functional provides a very good description of the colloid profiles, in particular the dramatic increase in the wall contact value as polymer is added [15]; the functional accounts

[5] In a very recent study of a similar mixture of silica particles and PDMS in cyclohexane the density difference and surface tension between coexisting phases were determined closer to the critical point than in [3]. Chen *et al* [16] report tensions <1 μN m^{-1} and a good fit to Ising-like scaling.

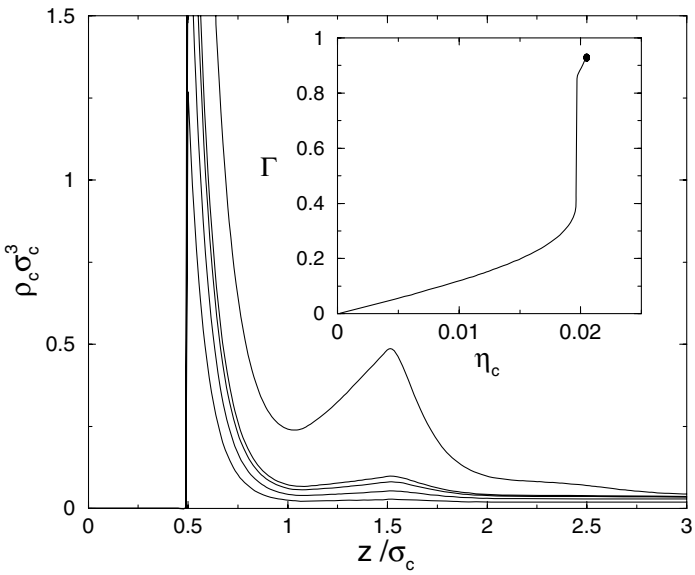

Figure 4. Colloid density profiles showing the layering transition at $\eta_p^r = 0.7$ corresponding to path II in figure 1. Bulk colloid fractions are $\eta_c = 0.010$, 0.015, 0.018, 0.019 and 0.020 (from bottom to top); the transition occurs between 0.019 and 0.020. The inset shows the Gibbs adsorption Γ which jumps at the transition and remains finite at bulk coexistence $\eta_c = 0.0203$.

for the depletion attraction between the wall and the colloids. Here we focus on larger size ratios where fluid–fluid demixing occurs. We fix η_p^r and approach the bulk phase boundary from the colloid-poor side.

Depending on the value of η_p^r chosen, the adsorption behaviour changes dramatically. As an example we consider the size ratio $q = 0.6$ and describe the phenomena encountered. We first choose a path just above the critical point, $\eta_p^r = 0.55$, see path I in figure 1. On approaching the phase boundary we find that the wall is completely wet by the colloid-rich phase. Figure 3 shows the colloid profiles signalling the growth of a thick layer of colloidal liquid against the wall[6]. The corresponding polymer profiles are shown in the inset and indicate how polymer becomes more depleted as the colloid-rich layer grows. At large values of η_p^r (>0.72) we find that the wall is only partially wet by colloid; the layer thickness increases continuously, remaining finite at bulk coexistence. At lower values ($0.62 < \eta_p^r < 0.72$) we find a first-order layering transition. This is illustrated in figure 4 where the colloid profiles are plotted for $\eta_p^r = 0.7$, following path II in figure 1 along with the Gibbs adsorption $\Gamma = \sigma_c^2 \int_0^\infty (\rho_c(z) - \rho_c(\infty))\,\mathrm{d}z$. At the transition the densities $\rho_c(z)$ in the first (contact) layer and in the second layer increase substantially and Γ jumps discontinuously. Γ remains finite at bulk coexistence, i.e. there is still partial wetting. The layering transition line ends in a critical point at $\eta_p^r \approx 0.62$ (see figure 5), below which the adsorption increases continuously as η_c increases towards its value at bulk coexistence. Further layering transitions can be located by calculating the density profiles *along* the coexistence curve. These are shown in figure 5. At the second transition a third adsorbed layer of colloid develops and the local density in the second layer increases significantly so that Γ jumps discontinuously. Similarly, at the

[6] Strictly speaking *macroscopically* thick wetting films can only occur on the monotonic side of the FW line, i.e. for $\eta_p^r < \eta_{p,\mathrm{FW}}^r$, since oscillatory binding potentials will stabilize very thick but finite films which would otherwise be infinite [17]. For $\eta_p^r = 0.55$ (path I) we can easily obtain films of thickness 20 or $30\sigma_c$.

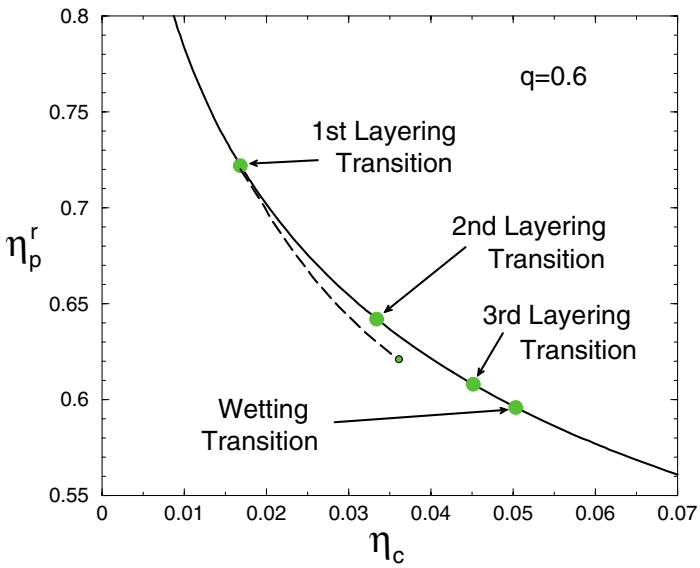

Figure 5. Surface phase diagram for the mixture at a hard wall. The full curve is a portion of the bulk coexistence curve of figure 1 and the circles denote the onset of three layering transitions. The first layering transition line (broken curve) extends deep into the single- (gas-) phase region, ending in a critical point near $\eta_p^r = 0.62$, whereas the second and third transition lines are extremely short. The transition from partial to complete wetting is denoted by the lowest circle and the accompanying pre-wetting line is also extremely short.

(This figure is in colour only in the electronic version)

third transition the fourth adsorbed layer develops with an accompanying increase in density of layer three, giving another jump in Γ. Unlike at the first transition the second and third transition lines are extremely short in η_p^r and as it is very difficult to determine these accurately we have simply represented the transitions as circles in figure 5. Below the third transition Γ remains finite at bulk coexistence until $\eta_p^r \sim 0.595$ where the transition to complete wetting occurs. This appears to be first order, i.e. Γ appears to diverge discontinuously. However, it is difficult to determine the prewetting line, which should emerge tangentially from the coexistence curve at the wetting transition. All we can say with certainty is that any prewetting line is extremely short[7].

This pattern of surface transitions is quite different from what is usually found for simple fluids adsorbed at strongly attractive substrates where, for temperatures not too far from the triple point, complete wetting often proceeds via a sequence (possibly infinite) of layering transitions [19] extending away from bulk coexistence. Here we have three layering transitions, only the first of which extends far into the single (gas) phase, occurring far from the triple point which is at $\eta_p^r \sim 1.43$ in the free-volume theory. Although there may be a fourth, fifth, etc, layering transition we are unable to detect these. The occurrence of such a pattern of transitions reflects the underlying difference between a one-component fluid, described by a simple pairwise fluid–fluid potential, and the present binary AO mixture, for which the effective one-component Hamiltonian [6] involves pairwise potentials which depend on the distance of the colloids from

[7] In a preliminary conference report of our results [18] we correctly identified the first layering transition line but failed to identify the second and third transitions and to determine accurately the wetting transition.

the wall as well as complex higher-body interactions[8]. How the pattern of surface transitions depends on the size ratio q will be described elsewhere [15] but we believe our present predictions of entropically driven wetting and layering transitions might encourage experimental investigations of adsorption in colloid–polymer mixtures. Real space techniques, such as confocal microscopy, should provide a useful tool for observing wetting in colloidal suspensions.

In summary we have shown that interfacial properties of the simplest model colloid–polymer mixture can be extremely rich. That such a diversity of phenomena should arise in a system where the bare interactions are either hard or ideal is remarkable and points to the importance of entropic depletion forces in determining surface as well as bulk phase behaviour.

We thank A J Archer, M Dijkstra, E H A de Hoog, A Gonzalez, J R Henderson, H N W Lekkerkerker, A O Parry and M M Telo da Gama for helpful discussions. We are the particularly grateful to R Roth for valuable advice on numerical matters and for carrying out an independent check of the surface phase diagram. This research was supported by the British–German ARC programme and by DFG Lo 418/5.

References

[1] See, e.g., Gast A P, Hall C K and Russel W B 1983 *J. Colloid. Interface. Sci.* **96** 251
Ilett S M *et al* 1995 *Phys. Rev.* E **51** 1344
Poon W C K, Pusey P N and Lekkerkerker H N W 1996 *Phys. World* **9** 27
[2] Asakura S and Oosawa F 1954 *J. Chem. Phys.* **22** 1255
[3] de Hoog E H A and Lekkerkerker H N W 1999 *J. Phys. Chem.* B **103** 5274
[4] de Hoog E H A *et al* 1999 *J. Phys. Chem.* B **103** 10 657
[5] Brader J M and Evans R 2000 *Europhys. Lett.* **49** 678
[6] Brader J M, Dijkstra M and Evans R 2001 *Phys. Rev.* E **63** 041405
[7] Vrij A 1997 *Physica* A **235** 120
[8] Vrij A 1976 *Pure Appl. Chem.* **48** 471
[9] Dijkstra M, Brader J M and Evans R 1999 *J. Phys.: Condens. Matter* **11** 10 079 and references therein
[10] Schmidt M, Löwen H, Brader J M and Evans R 2000 *Phys. Rev. Lett.* **85** 1934
[11] Lekkerkerker H N W *et al* 1992 *Europhys. Lett.* **20** 559
[12] Rosenfeld Y 1989 *Phys. Rev. Lett.* **63** 980
Tarazona P and Rosenfeld Y 1997 *Phys. Rev.* E **55** R4873
Rosenfeld Y *et al* 1997 *Phys. Rev.* E **55** 4245
[13] Evans R *et al* 1994 *J. Chem. Phys.* **100** 591
[14] Evans R *et al* 1993 *Molec. Phys.* **80** 755
[15] Brader J M 2001 *PhD Thesis* University of Bristol
[16] Chen B-H, Payandeh B and Robert M 2000 *Phys. Rev.* E **62** 2369
[17] Henderson J R 1994 *Phys. Rev.* E **50** 4836
[18] Evans R *et al* 2001 *Phil. Trans. R. Soc.* A **359** 961
[19] See, e.g., Ball P C and Evans R 1988 *J. Chem. Phys.* **89** 4412 and references therein

[8] We have confirmed this assertion by investigating adsorption at a hard wall for $q = 0.6$, using the DFT described in [6], for a one-component fluid given by the AO pair potential at a wall which exerts the AO wall–fluid depletion potential. No layering transitions are found.