



Very low surface tension liquid–vapour interfaces of patchy colloids



P.I.C. Teixeira^{a,b,*}

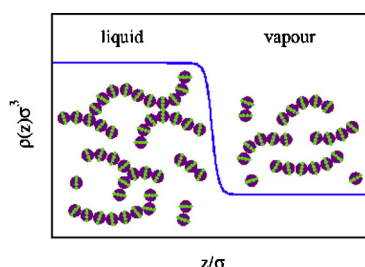
^a ISEL – Instituto Superior de Engenharia de Lisboa, Instituto Politécnico de Lisboa, Rua Conselheiro Emídio Navarro 1, 1959-007 Lisbon, Portugal

^b Centro de Física Teórica e Computacional, Faculdade de Ciências da Universidade de Lisboa, Campo Grande, Edifício C8, 1749-016 Lisbon, Portugal

HIGHLIGHTS

- A simple local density-functional theory of 2AnB patchy colloids is proposed.
- It is applied to the liquid–vapour interface of this system.
- It predicts a surface tension that varies non-monotonically with temperature.
- 2AnB colloids might be used as temperature-controlled surfactants, foam stabilizers.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 23 September 2016

Received in revised form 3 November 2016

Accepted 13 November 2016

Available online 21 November 2016

PACS:

64.70.F–

68.03.–g

64.75.Yz

Keywords:

Patchy colloids

Liquid–vapour transition

Interfacial properties

ABSTRACT

The liquid–vapour interface of a model of one-component patchy colloids is re-visited. The model consists of hard spheres decorated with short-ranged attractive sites ('patches') of different types on their surfaces. In an earlier paper [A. Oleksy and P.I.C. Teixeira, *Phys. Rev. E* 91 (2015) 012301], the density-functional theory (DFT) form of Wertheim's first-order perturbation theory (TPT1) was used to study a realisation of this model with two patches of type *A* and nine patches of type *B* (2A9B colloids), which exhibit re-entrant liquid–vapour coexistence curves and very low-density liquid phases. Here, it is shown that the non-monotonic temperature dependence of the surface tension and interface thickness in this model can be qualitatively reproduced by a local DFT, where the spatial non-uniformity is introduced through the square gradient of the density multiplied by a density-dependent prefactor. This simpler theory is then applied to colloids decorated with two patches of type *A* and ten patches of type *B* (2A10B colloids), and interactions chosen so as to exhibit a closed-loop phase diagram when only *AA* and *AB* bonds are present [N.G. Almarza et al., *J. Chem. Phys.* 137 (2012) 244902]. In this case, the surface tension goes to zero at both upper and lower critical points, with a maximum at some intermediate temperature. As *BB* attractions are gradually switched on, the lower critical point disappears and the surface tension vs temperature curve acquires a very deep minimum at a temperature lower than that of the maximum. On further increasing the strength of the *BB* attractions, both the minimum and the maximum disappear and the surface tension becomes a monotonically decreasing function of the temperature, as in atomic fluids. The very low surface tension at the minimum for weak *BB* attractions, combined with the ability to form physical gels, suggests that 2AnB colloids might be exploited as temperature-controlled surfactants and foam stabilizers.

© 2016 Elsevier B.V. All rights reserved.

* Correspondence to: Centro de Física Teórica e Computacional, Faculdade de Ciências da Universidade de Lisboa, Campo Grande, Edifício C8, 1749-016 Lisbon, Portugal.

E-mail address: pিতেixeira@fc.ul.pt

URL: <http://webpages.fc.ul.pt/pিতেixeira>.

1. Introduction

Patchy colloids are a conceptually simple model for studying the interplay between phase separation (namely condensation) and self-assembly in soft matter. Their simplest realisation is as hard spherical particles decorated with discrete attractive sites ('patches') on their surfaces. Though they were originally introduced as a theoretical construct [1–7] patchy colloids have since been synthesized by a variety of methods [8–10].

The bulk phase behaviour of patchy colloids with all identical patches is determined by the (mean) number of patches M per particle: when $M \rightarrow 2^+$, both the liquid–vapour critical density and the critical temperature become vanishingly small, and for $M \leq 2$ condensation disappears altogether [11,12]. The case of patches of two different types (A and B) has been extensively studied using Wertheim's first-order thermodynamic perturbation theory of association (TPT1) [13–17]. Now three types of bonds are possible: AA bonds promote aggregation into linear chains, while BB and AB bonds give rise, respectively, to X -junctions (connecting two interior particles of a chain) and Y -junctions (connecting the end of one chain to an interior particle of another chain). If AA bonds are the strongest, then the ground state (zero-temperature) of the system consists of infinite linear chains. At finite temperatures there will be defects, which can be chain ends, X -junctions or Y -junctions. When Y -junctions are the dominant defect, the liquid–vapour binodal is re-entrant and a very low-density liquid (sometimes termed an 'empty liquid') will co-exist with the vapour, well below the critical temperature. Such liquid states consist of long chains of AA -bonded particles, occasionally branching at AB bonds.

In a recent paper [18], we used the density-functional theory (DFT) form of TPT1, as implemented by Yu and Wu [19], to calculate the structure and thermodynamics of the liquid–vapour interface of patchy colloids with two sites of type A and nine sites of type B ($2A9B$ colloids). We confirmed the earlier prediction of Bernardino and Telo da Gama [20] that, for a choice of parameters such that the phase diagram is re-entrant as described above, the surface tension vs temperature curve has a maximum. However, we found, in addition, that the thickness of the liquid–vapour interface also varies non-monotonically: it first decreases on going down in temperature from the critical point, but then increases again as the temperature is lowered further into the re-entrant region of the phase diagram. This can be understood by recalling that the interfacial thickness is a measure of the bulk correlation length ξ [21]: in the re-entrant region, both coexisting phases are fairly rich in aggregates (branched chains in the liquid, linear chains in the vapour) whose characteristic size diverges as $T \rightarrow 0$.

In this paper I show that qualitatively the same results for the interfacial properties of patchy colloids can be obtained using a much simpler version of DFT that employs a local approximation for the free energy and where the density non-uniformity is introduced via a simple square-gradient term. Crucially, the coefficient of this square-gradient term must itself be a function of the local density, as in theories of polymers. I apply this simplified theory to an extreme case of re-entrance where there are two liquid–vapour critical points if only AA and AB interactions are present. As BB interactions are gradually switched on, the lower critical point is lost and the liquid branch of the binodal first acquires the familiar re-entrant shape. Sufficiently strong BB interactions remove this feature and the phase diagram becomes similar to that of an atomic fluid. The above behaviour is reflected in the temperature dependence of the surface tension, which can have both a maximum and a minimum for weak BB interactions. This opens up the possibility of using patchy colloids as temperature-controlled surfactants.

This paper is organized as follows: in Section 2 I describe the model used and give details of the theory. Then in Section 3 I present

my results and compare them with those of earlier theories [18,20]. Finally I conclude in Section 4.

2. Model and density-functional theory

2.1. Model: $2AnB$ colloids

As in earlier work [15–18], I consider a one-component fluid of N hard spheres (HSs) of diameter σ and volume $v_s = (\pi/6)\sigma^3$, each decorated on its surface with two patches of type A and n patches of type B . This will be referred to henceforth as $2AnB$ colloids. The interparticle pair potential is a combination of HS repulsion and square-well attraction between the surface patches. The attraction between patch α on particle i and patch β on particle j is given by the Kern–Frenkel potential [22]:

$$V_{ij,\alpha\beta} = V_{\alpha\beta}^{SW}(r_{ij})G(\hat{\mathbf{r}}_{ij}, \hat{\mathbf{r}}_{\alpha i}, \hat{\mathbf{r}}_{\beta j}), \quad (1)$$

where $V_{\alpha\beta}^{SW}$ is a square-well potential,

$$V_{\alpha\beta}^{SW}(x) = \begin{cases} \infty & \text{if } x < \sigma \\ -\epsilon_{\alpha\beta} & \text{if } \sigma < x < \sigma + \delta_{\alpha\beta} \\ 0 & \text{otherwise,} \end{cases} \quad (2)$$

and $G(\hat{\mathbf{r}}_{ij}, \hat{\mathbf{r}}_{\alpha i}, \hat{\mathbf{r}}_{\beta j})$ is the angle-dependent part,

$$G(\hat{\mathbf{r}}_{ij}, \hat{\mathbf{r}}_{\alpha i}, \hat{\mathbf{r}}_{\beta j}) = \begin{cases} 1 & \left\{ \begin{array}{l} \text{if } \hat{\mathbf{r}}_{ij} \cdot \hat{\mathbf{r}}_{\alpha i} > \cos \theta_{\alpha\beta}^{\max} \\ \text{and } -\hat{\mathbf{r}}_{ij} \cdot \hat{\mathbf{r}}_{\beta j} > \cos \theta_{\alpha\beta}^{\max} \end{array} \right. \\ 0 & \text{otherwise.} \end{cases} \quad (3)$$

Here $\hat{\mathbf{r}}_{ij}$ is the unit vector along the axis defined by the centres of particles i and j , and $\hat{\mathbf{r}}_{\alpha i}$ is the unit vector pointing from the centre of particle i to the centre of patch α on its surface. The model is thus specified by three sets of parameters: the interaction energies between patches $\epsilon_{\alpha\beta}$, their ranges $\delta_{\alpha\beta}$, and the patch opening angles $\theta_{\alpha\beta}^{\max}$. Together the ranges and opening angles set the volume $v_b^{\alpha\beta}$ available to each type of bond:

$$v_b^{\alpha\beta} = \frac{\pi}{3} [(\sigma + \delta_{\alpha\beta})^3 - \sigma^3] (1 - \cos \theta_{\alpha\beta}^{\max})^2. \quad (4)$$

The bond volumes are set such that each patch can only interact with one other patch at a time, and it is assumed that the distribution of patches on the particle's surface only allows single bonding between any pair of particles. Imposing these conditions ensures that the system satisfies the assumptions of Wertheim's TPT1 [1,2,5].

2.2. Theory: square-gradient approximation

Unlike in [18], where the full armoury of DFT was brought to bear on the interfacial properties of $2AnB$ colloids, here I seek the much simpler, but qualitatively correct, description afforded by the square-gradient approximation [21]:

$$F[\rho(\mathbf{r})] = \int \left\{ f_{id}[\rho(\mathbf{r})] + f_{hs}[\rho(\mathbf{r})] + f_b[\rho(\mathbf{r}), X_A(\mathbf{r}), X_B(\mathbf{r})] + f_2[\rho(\mathbf{r})][\nabla\rho(\mathbf{r})]^2 \right\} d\mathbf{r}, \quad (5)$$

where $\rho(\mathbf{r})$ is the number density profile, and $X_\alpha(\mathbf{r})$ is the spatially-varying fraction of unbonded sites of type α . The coefficient of the square-gradient term is given by [21]

$$f_2(\rho) = \frac{k_B T}{12} \int r^2 c(\mathbf{r}; \rho) d\mathbf{r}, \quad (6)$$

where k_B is Boltzmann's constant, T is the temperature, and $c(\mathbf{r}; \rho)$ is the direct correlation function (DCF) of the fluid. The DCF of $2AnB$

Download English Version:

<https://daneshyari.com/en/article/4982434>

Download Persian Version:

<https://daneshyari.com/article/4982434>

[Daneshyari.com](https://daneshyari.com)