Liquid-vapour interfaces of patchy colloids

Paulo Teixeira

ISEL – Instituto Superior de Engenharia de Lisboa, Instituto Politécnico de Lisboa and Centro de Física Teórica e Computacional, Faculdade de Ciências, Universidade de Lisboa
Lisbon, Portugal
In general, interactions between atoms, molecules or ions comprise a short-range repulsion and a longer-ranged attraction. In the Van der Waals picture, the interplay of interaction energy and entropy – expressed as free energy – determines which phases are realised.

- At low temperatures/high densities energy wins and we have a condensed phase – a liquid or a solid.
- At high temperatures/low densities entropy wins and we have a dilute phase – a gas.
Most molecular species have permanent dipoles.

Criticality of strongly dipolar fluids is still unsolved problem (image by J.-J. Weis).

A related, more general issue is interplay between condensation and association.

We want to study a model that retains the essential symmetry of dipolar forces leading to association, but leaves out apparently inessential features (long range and complex angular dependence).
**Patchy colloids**

- **Patchy colloids** are custom-fabricated matter that exhibits both self-assembly and the usual phase transitions (condensation, freezing, etc) (images by Y. S. Cho *et al.*).


![Graphs and diagrams showing phase transitions and simulation results for patchy colloids.](Images)
Model: 2AnB patchy colloids

- Hard spheres (HSs) of diameter \( \sigma \) and volume \( v_s \), each decorated with two A and n B patches. AA, BB or AB bonds may form.

- AA bonds give linear chains.

- BB bonds give X-junctions, always energetically favourable: \( \epsilon_j = -\epsilon_{BB} < 0 \).

- AB bonds give Y-junctions, energetically favourable only if \( \epsilon_{AB}/\epsilon_{AA} > 1/2 \).

- X- and Y-junctions yield different L-V phase behaviours.
Theory for bulk

- **Bonding free energy** from Wertheim’s TPT1:

\[
\beta f_b \equiv \frac{\beta F_b}{N} = 2 \ln X_A + n \ln X_B - X_A - \frac{nX_B}{2} + \frac{2 + n}{2}
\]

\(X_\alpha\) is the probability of having a sticky spot of type \(\alpha\) not bonded.

- **Laws of mass action** are

\[
X_A + 2\eta \Delta_{AA} X_A^2 + m\eta \Delta_{AB} X_A X_B = 1 \\
X_B + m\eta \Delta_{BB} X_B^2 + 2\eta \Delta_{AB} X_A X_B = 1,
\]

with packing fraction \(\eta \equiv (N/V)v_s\) and **bond partition function**

\[
\Delta_{\alpha\beta} = 4\pi \int_{\nu_{\alpha\beta}} g_{\text{ref}}(r_{12}) \langle \exp \left[ -\beta \phi_{\alpha\beta}(r_{12,\alpha\beta}) \right] - 1 \rangle_{\omega_1,\omega_2} r_{12}^2 dr_{12}
\]

- **Free energy per particle** is a function of \((\eta, T)\) only:

\[
\beta f = \beta f_{HS} + \beta f_b
\]
Interpatch potential

- **Spherical square wells (SW) centred on patches:**

\[
\phi_{12,\alpha\beta}(\mathbf{r}_{12}, \hat{\mathbf{r}}_{\alpha 1}, \hat{\mathbf{r}}_{\beta 2}) = \phi^{SW}(\mathbf{r}_{12,\alpha\beta})
\]

with \( \mathbf{r}_{12,\alpha\beta} \) the vector connecting the centre of patch \( \alpha \) on particle 1 to the centre of patch \( \beta \) on particle 2:

\[
\mathbf{r}_{12,\alpha\beta} = \mathbf{r}_2 + \sigma \hat{\mathbf{r}}_{\beta 2} - \mathbf{r}_1 - \sigma \hat{\mathbf{r}}_{\alpha 1}
\]

- **Alternatively, Kern-Frenkel potential:**

\[
\phi_{12,\alpha\beta}(\mathbf{r}_{12}, \hat{\mathbf{r}}_{\alpha 1}, \hat{\mathbf{r}}_{\beta 2}) = \phi^{SW}_{\alpha\beta}(\mathbf{r}_{12}) G(\hat{\mathbf{r}}_{12}, \hat{\mathbf{r}}_{\alpha 1}, \hat{\mathbf{r}}_{\beta 2})
\]

\[
G(\hat{\mathbf{r}}_{12}, \hat{\mathbf{r}}_{\alpha 1}, \hat{\mathbf{r}}_{\beta 2}) = \begin{cases} 
1 & \text{if } \hat{\mathbf{r}}_{12} \cdot \hat{\mathbf{r}}_{\alpha 1} > \cos \theta_{\alpha\beta}^{\text{max}} \\
0 & \text{and } -\hat{\mathbf{r}}_{12} \cdot \hat{\mathbf{r}}_{\beta 2} > \cos \theta_{\alpha\beta}^{\text{max}} \\
& \text{otherwise.}
\end{cases}
\]

\[
\phi^{SW}_{\alpha\beta}(x) = \begin{cases} 
\infty & \text{if } x < \sigma \\
-\epsilon_{\alpha\beta} & \text{if } \sigma < x < \sigma + \delta_{\alpha\beta} \\
0 & \text{otherwise,}
\end{cases}
\]
Summary of results for bulk

- If $\epsilon_{AA} = 0$ there is no critical point.
- If $\epsilon_{AB} = 0$, critical point exists all the way down to $\epsilon_{BB}/\epsilon_{AA} = 0$. This is X-junction condensation.
- If $\epsilon_{BB} = 0$, define $C = \frac{2(B_2^{hs})^2 v_{AA}}{(nv_{AB})^3}$:
  - If $C > 1$:
    - $\epsilon_{AB}/\epsilon_{AA} > 1/3$: a single critical point; liquid-vapour binodal is re-entrant for $1/3 < \epsilon_{AB}/\epsilon_{AA} < 1/2$.
    - $\epsilon_{AB}/\epsilon_{AA} < 1/3$: no critical point.
  - If $C < 1$:
    - $\epsilon_{AB}/\epsilon_{AA} > 1/3$: a single critical point; liquid-vapour binodal is re-entrant.
    - $r_m < \epsilon_{AB}/\epsilon_{AA} < 1/3$: two critical points.
    - $\epsilon_{AB}/\epsilon_{AA} < r_m$: no critical point.

Whenever it exists, this is Y-junction condensation.

- By changing the ratio of interaction strengths, we are able to engineer very low density liquid phases: ‘empty liquids’.
- Different cluster structures may result, percolated or not.
- What about L-V interfaces? Most interesting for empty liquids.
Types of L-V phase diagrams

Regular

Re-entrant

Closed loop
Helmholtz free energy (FE) functional is sum of three contributions:

\[ F[\rho(r)] = F_{id}[\rho(r)] + F_{hs}[\rho(r)] + F_b[\rho(r), \{X_\alpha(r)\}] \]

\( \rho(r) \) is number density profile, \( X_\alpha(r) \) is fraction of unbonded \( \alpha \) sites.

Translational entropy of ideal system (exact):

\[ F_{id}[\rho(r)] = k_B T \int d\mathbf{r} \rho(r) \left\{ \ln \left[ \Lambda^3 \rho(r) \right] - 1 \right\} \]

Fundamental-measure theory (FMT) approximation to HS FE:

\[ F_{hs}[\rho(r)] = \int d\mathbf{r} \Phi_{hs}[\{n_i(\mathbf{r})\}] \]

\( \{n_i(\mathbf{r})\} \) are coarse-grained densities.

Bonding free energy from Wertheim’s TPT1:

\[ F_b = \int dz \ n_0(\mathbf{r}) \left[ 1 - \frac{n_{v2}(\mathbf{r}) \cdot n_{v2}(\mathbf{r})}{n_2^2(\mathbf{r})} \right] \times \left\{ 2 \ln X_A(\mathbf{r}) - X_A(\mathbf{r}) + \frac{1}{2} \right\} + n \left[ \ln X_B(\mathbf{r}) - X_B(\mathbf{r}) + \frac{1}{2} \right] \]
Theory for interfaces II

- Plus laws of mass action:

\[
X_A(r) = \left\{ 1 + n_0(r) \left[ 1 - \frac{n_{V2}(r) \cdot n_{V2}(r)}{n_2^2(r)} \right] \right\}^{-1} \left[ 2X_A(r)\Delta_{AA}(r) + nX_B(r)\Delta_{AB}(r) \right]
\]

\[
X_B(r) = \left\{ 1 + n_0(r) \left[ 1 - \frac{n_{V2}(r) \cdot n_{V2}(r)}{n_2^2(r)} \right] \right\}^{-1} \left[ 2X_A(r)\Delta_{AB}(r) + nX_B(r)\Delta_{BB}(r) \right]
\]

\[
\Delta_{\alpha\beta}(r) = 4\pi \frac{V_{\alpha\beta}}{v_{hs}} g^h_s(n_2, n_3) \exp(\epsilon_{\alpha\beta}/k_B T) - 1
\]

- Minimise grand-canonical potential to get \( \rho(z), X_\alpha(z) \):

\[
\Omega[\rho(r)] = F[\rho(r)] + \int dr \left[ V_{\text{ext}}(r) - \mu \right] \rho(r)
\]

\[
\frac{\delta \Omega[\rho(r)]}{\delta \rho(r)} = 0 \iff \frac{\delta F[\rho(r)]}{\delta \rho(r)} = \mu - V_{\text{ext}}(r)
\]
Results for 2A9B model: $\epsilon_{BB} = 0$, variable $\epsilon_{AB}$

**Phase diagram and surface tension**

- **Re-entrant** L-V phase diagram if $\epsilon_{BB} = 0$ and $1/3 < \epsilon_{AB}/\epsilon_{AA} < 1/2$.
- **Ground state** is long chains, Y-junctions appear at higher $T$.
- **Non-monotonic** surface tension vs $T$ if phase diagram is re-entrant.

Results for $2A9B$ model: $\epsilon_{BB} = 0$, variable $\epsilon_{AB}$

Density profiles

$\epsilon_{AB} = 0.40\epsilon_{AA}$

- If L-V phase diagram is re-entrant, L-V interface thickens at low $T$.
- Interfacial thickness is measure of bulk correlation length. In re-entrant region, size of aggregates (branched chains in the liquid, linear chains in the vapour) diverges as $T \rightarrow 0$.

Results for 2A9B model: $\epsilon_{BB} = 0$, variable $\epsilon_{AB}$

Snapshot of vapour and liquid phases for $\epsilon_{AB} = 0.37\epsilon_{AA}$

MC simulations by L. Rovigatti and F. Sciortino
Results for 2A9B model: $\epsilon_{AB} = 0.35\epsilon_{AA}$, variable $\epsilon_{BB}$

Phase diagram and surface tension

- X-junctions dominate at low $T$, Y-junctions close to $T_c$.
- In intermediate range of $\epsilon_{BB}$ surface tension vs $T$ may have both a maximum and a minimum.

Results for 2A9B model: $\epsilon_{AB} = 0.35\epsilon_{AA}$, variable $\epsilon_{BB}$

Density profiles

$\epsilon_{BB} = 0.30\epsilon_{AA}$

- Switching on $\epsilon_{BB}$ restores “normal” fluid behaviour (no thickening at low $T$).
- In intermediate range of $\epsilon_{BB}$ interface thickness vs $T$ can have both a maximum and a minimum.

And now for something completely different: Helmholtz FE functional given by square-gradient approximation:

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

Physically motivated Ansatz: at low enough temperature and for \( \epsilon_{AA} > \epsilon_{AB}, \epsilon_{BB} \), liquid and vapour phases resemble polymer melts:

\[
f_2(\rho) = \frac{k_B T \tilde{M}}{2\rho},
\]

The Euler-Lagrange equation for \( \rho(z) \) is then

\[
\beta (\mu_{id} + \mu_{hs} + \mu_b) + \frac{\tilde{M}}{2\rho(z)^2} \left[ \frac{d\rho(z)}{dz} \right]^2 - \frac{\tilde{M}}{\rho(z)} \frac{d^2 \rho(z)}{dz^2} = \beta \mu
\]

At each \((\rho, T)\), \(X_A\) and \(X_B\) are given by the bulk laws of mass action.
Results for 2A9B model: $\epsilon_{AB} = 0.36\epsilon_{AA}$, variable $\epsilon_{BB}$

Phase diagram and surface tension

- In intermediate range of $\epsilon_{BB}$ surface tension vs $T$ does indeed have both a maximum and a minimum.

Results for 2A9B model: $\epsilon_{AB} = 0.36 \epsilon_{AA}$, variable $\epsilon_{BB}$

**Density profiles**

$$\epsilon_{BB} = 0.20 \epsilon_{AA}$$

- Switching on $\epsilon_{BB}$ restores “normal” fluid behaviour (no thickening at low $T$).
- In intermediate range of $\epsilon_{BB}$ interface thickness vs $T$ can have both a maximum and a minimum.

Results for 2A10B model: $\epsilon_{AB} = 0.25\epsilon_{AA}$, variable $\epsilon_{BB}$

Phase diagram and surface tension

- In cases of extreme re-entrance, $\epsilon_{BB}$ surface tension can be vanishingly small in a narrow range of $T$.

Summary and conclusions

- We have studied the L-V interface of a model of colloids with $A$ and $B$ patches, using the DFT form of Wertheim's TPT1, combined with FMT.
- Density $\rho(z)$ and fractions of unbonded $A$ or $B$ patches, $X_A(z)$ and $X_B(z)$, respectively, vary monotonically with $z$.
- Interfacial thickness and surface tension can be non-monotonic functions of temperature if L-V binodal is re-entrant.
- Combining bulk TPT1 with a simple square-gradient approximation with a density-dependent gradient prefactor gives qualitatively the same results. This appears reliable if non-uniformity is moderate.
- If L-V re-entrance is extreme, the surface tension can be very low in a narrow range of temperatures: $2AnB$ colloids might be used as temperature-controlled surfactants and foam stabilisers.
- The present theory should be applicable to same model fluid at a wall or in confinement, but not at low temperatures because the theory averages over patch positions.
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