Understanding the Phase Diagram of Dipolar Hard Spheres

Joao Guilherme Ferreira Campos

January 10, 2016

Abstract

In this work, we investigate the phase diagram of the liquid-gas transition in dipolar hard-spheres and the existence of a critical point. Two different methods are employed: a coarse-grained mean-field analysis and a microscopic Thermodynamic Perturbation Theory. The coarse-grained theory explores the fact that dipolar hard-spheres aggregate in chains at low temperatures. On the other hand, The Thermodynamic Perturbation theory is applied to a patchy particle model, which allows analytical treatment. This model is chosen such that it self-assembles with the same topology of the dipolar hard-spheres, at low temperatures. We find evidence of the existence of a critical point, at low temperature and low density, with a pinched shape phase diagram. However, The critical point may vanish depending on the energy cost of defects. Moreover, we show that complex systems can be understood by studying simpler systems with the same microscopic properties which are more suitable to numerical and analytical analyses.
1 Introduction

Isotropic fluids with excluded-volume repulsion and long-range attraction present a liquid-gas phase transition (LGT). This transition is well known have been exhaustively studied both analytically and numerically. There, the competition between the energy loss of a high-density liquid and the entropy gain a low-density gas allows the coexistence of the two phases and the existence of a critical point [1]. However, these systems are not so interesting because they only aggregate in isotropic clusters. On the other hand, anisotropic fluids are able to self-assemble in complex aggregates such as chains, mycelles and vesicles, but much effort is still needed to understand such interactions.

A particularly interesting anisotropic system is formed by Dipolar Hard-Spheres (DHS). It is of the simplest model of highly directional liquids and it can be used to model ferrofluids and electro-rheological fluids. Dipolar particles tend to align and form chains and recently a coarse-grained mean-field analysis showed that its coexistence curve has a pinched shape as a result of a competition between chaining defects at low temperatures [4]. Moreover, there has been great theoretical evidence of such a critical point, but it has been difficult to observe such coexistence curve numerically because the critical point lies at very low temperature and density, where typical simulation methods have very slow convergence.

To investigate numerically such coexistence curve, a patchy particle model has been proposed [14], [15]. Patchy particles are composed of a hard-core with directional sticky points and are a powerful tool to understand fluids. In particular, they are accurately described by a Thermodynamic Perturbation Theory developed by Wertheim [9], [10], [11]. Moreover, patchy particles are particularly suitable to numerical treatment, due to the simplicity of the system, and to experimental treatments, due to recent advances in coloidal synthesis. They can be used to study DHS because, if the properties and the number of the sticky points are tuned accordingly, the patchy particles self-assemble with the same topology as DHS at low temperatures.

Here, the coarse-grained theory and the Wertheim’s theory are reviewed and the parallel between Patchy particles and DHS is dicussed. The rest of the work is organized as follows: In Section 2 we review the LGT in isotropic fluids and its coexistence curve, in section 3 we present a coarse-grained mean-field analysis of DHS fluids, in section 4 we show how to use a patchy particle model and Wertheim’s theory to understand the DHS coexistence curve and in section 5 we summarize our conclusions.

2 Isotropic Fluids

Here, we describe a mean-field analysis of a lattice model of the liquid-gas transition\(^1\). The liquid-gas transition is a first-order phase transition and it is reasonably well described by mean-field theories, which neglects correlations. However, the order parameter of the liquid-gas transition vanishes at a critical temperature \(T_c\) and a critical concentration \(\phi_c\), characterizing a second order phase transition. Near this point, correlations diverge and, therefore, the mean-field theory breaks down. On the other hand, a coarse-grained description, such as a lattice model to describe liquids, describes only the large scale behaviour. Small scale behaviour is not relevant to describe a second order phase transition, but it cannot be neglected in a quantitative

\(^1\)We follow section 4.1 in [1].
Figure 1: (left) Energetic (concave) and Entropy (convex) contributions to the free energy. (right) Typical free energy landscape for $T > T_c$ and $T < T_c$, the common tangent construction is also shown. Extracted from [1].

accurate description of first order phase transitions. Nonetheless, coarse-grained descriptions of a first order phase transition may give qualitative correct results and give intuition to the problem. The purpose of this section is to illustrate key concepts of the liquid-gas transition such as the coexistence curve, the order parameter, a mean-field theory and a coarse-grained description.

Consider a lattice containing $N$ sites and coordination number $\nu$. We start considering a binary mixture, where each site is occupied by either a molecule $A$ or a molecule $B$. We define a variable $n_i$ for each lattice site, such that $n_i = 0$ ($n_i = 1$) when the site $i$ contains a molecule $A$ ($B$). Nearest neighbour molecules interact with energies $-\epsilon_{AA}$, $-\epsilon_{BB}$ and $-\epsilon_{AB}$ according to the species present in the interacting sites. The Hamiltonian is given by

$$H(\{n_i\}) = -\sum_{(i,j)} \epsilon_{AA}(1-n_i)(1-n_j) + \epsilon_{AB}(1-n_i)n_j + \epsilon_{AB}n_i(1-n_j) + \epsilon_{BB}n_in_j,$$  

(1)

where $(i,j)$ denotes sum over the $N\nu/2$ nearest neighbour pairs. We can be rewrite the hamiltonian as

$$H(\{n_i\}) = \epsilon \sum_{(i,j)} n_i(1-n_j) - 2B \sum_i n_i + C,$$  

(2)

where $\epsilon = \epsilon_{AA} + \epsilon_{BB} - 2\epsilon_{AB}$, $B = -\nu(\epsilon_{AA} - \epsilon_{BB})/4$ and $C = -N\nu\epsilon_{AA}/2$.

We define the concentration

$$\phi = \frac{1}{N} \langle \sum_i n_i \rangle$$  

(3)

and we compute the free energy (per particle) $f = (U - TS)/N$ using the brag williams mean-field argument. Assuming sites to be uncorrelated, the entropy is given by the entropy of mixing two ideal gases

$$S = -Nk_B[\phi \ln \phi + (1 - \phi) \ln(1 - \phi)].$$  

(4)
Note that the entropy is concave function of $\phi$, with a maximum at $\phi = \phi_c = 1/2$ (fully mixed system), favoring mixing (see Fig. 1). To simplify the derivation we assume the system to be symmetric under the exchange $A \leftrightarrow B$, that is, we set $\epsilon_{AA} = \epsilon_{BB}$. Thus, neglecting correlations, we have, up to a constant

$$U = \epsilon \sum_{(i,j)} \langle n_i \rangle (\langle 1 - n_i \rangle) = \frac{N \mu \epsilon}{2} \phi (1 - \phi). \quad (5)$$

Note that, only if $\epsilon > 0$, the energy is a concave function of $\phi$, with a maximum at $\phi = \phi_c = 1/2$, favoring demixing (see Fig. 1). Therefore, we assume $\epsilon > 0$ to ensure competition between energetic and entropic terms and phase separation. Putting the two terms together, we have that

$$f = \frac{\epsilon}{2} \phi (1 - \phi) + k_B T [\phi \ln \phi + (1 - \phi) \ln (1 - \phi)]. \quad (6)$$

Therefore, for low enough temperatures the free energy will have two minima $\phi_1$ and $\phi_2 > \phi_1$ and the for any concentration $\phi_1 < \phi < \phi_2$ the system can phase separate in an A-rich phase, with concentration $\phi_1$, and a B-rich phase with concentration $\phi_2$ (see Fig. 1).

The composition of the mixture is given by the minimum of the Grand Potential $\Sigma = f - \mu \phi$, where $\mu = \mu_A - \mu_B$. Minimizing with the respect to the concentration gives:

$$\mu = \left( \frac{\partial f}{\partial \phi} \right)_T. \quad (7)$$

and together with Eq. 6, we find that

$$\phi = \frac{1}{2} \left[ 1 + \tanh \left( \frac{\beta}{2} \left( \mu + \epsilon \nu \left( \phi - \frac{1}{2} \right) \right) \right) \right]. \quad (8)$$

The chemical potential is given by the common tangent construction, but due to the symmetry of the system $\mu = 0$ (see Fig. 1). Defining $x = \phi - 1/2$, we have

$$x = \frac{1}{2} \tanh \left( \frac{\beta \epsilon \nu}{2} x \right), \quad (9)$$

where you recognize the critical temperature $T_c = \epsilon \nu / 4 k_B$. Note that $x$ (or the difference between the concentrations $\phi - (1 - \phi) = 2x$) is the usual order parameter in analogy to the magnetization in ferromagnetic systems. However, the phase diagram is usually plotted as a function of the concentration $\phi$, which is a more intuitive parameter.

The coexistence curve, which is the solution of Eq. 8 with $\mu = 0$, and the spinodal curve, defined as the points at which $\frac{\partial^2 f}{\partial \phi^2} = 0$ are shown in Fig. 2. Between the coexistence curve and the spinodal curve the system is metastable and below the spinodal curve the system is unstable and the two lines meet at the critical point. The liquid-gas transition can be solved analogously, when you consider the asymmetric case where the $A$ molecules are vacancies, that is, when $\epsilon_{AA} = \epsilon_{AB} = 0$, but it is harder to plot the coexistence curve in this case, because the common tangent construction is not as trivial as before. In this case, You must first compute the pressure and then perform Maxwell’s construction. Typical phase diagrams of a Van der Waals fluid [3] (computed analytically) and a Lennard-Jones fluid [2] (computed using Monte Carlo simulations) are shown in Fig. 3. Observe that both Fig. 2 and 3 are similar in the sense that, as the temperature decreases, the gas concentration decreases approaching zero, while the liquid concentration increases.
Figure 2: Phase Diagram of a binary mixture. The full line is the Coexistence Curve and the dashed curve is the Spinodal Curve. The two lines meet in the critical point. Extracted from [1].

Figure 3: (a) Coexistence Curve of a Van der Waals fluid computed analytically (heavy line). Extracted from [3]. (b) Coexistence Curve of a Lennard-Jones Fluid computed using Monte Carlo Simulations. Extracted from [2]
3 Dipolar Hard-Spheres

Here, we investigate a coarse-grained mean-field theory to compute the phase diagram of DHS. Hard-Spheres (HS) interact via the following potential

\[
V_{HS} = \begin{cases} 
\infty & r < \sigma \\
0 & 0 \leq r > \sigma 
\end{cases}
\]  \hspace{1cm} (10)

where \( \vec{r} \) is the distance between two particles and \( \sigma \) is the HS diameter. The dipolar interaction is given by

\[
V_D = \frac{1}{r^3}(\vec{\mu}_1 \cdot \vec{\mu}_2) - \frac{3}{r^5}(\vec{\mu}_1 \cdot \vec{r})(\vec{\mu}_2 \cdot \vec{r})
\]  \hspace{1cm} (11)

where \( \mu_1 \) and \( \mu_2 \) are the dipoles momenta of the two interacting particles. The total potential interaction is given by \( V = V_{HS} + V_D \). We define the energy unit as \( u_d = \mu^2/\sigma^3 \) and the reduced temperature as \( T^* = k_B T/u_d \). When the two particles are in head-to-tail alignment \( V_{HS} = -2u_d \) which is twice the energy of side-by-side alignment (see Fig. 4A).

The anisotropic dipolar interactions favors nose-to-tail alignment of the HSs (see Fig. 4C). This drives the particles to self assemble in polymer-like chains, which is a one-dimensional process where no phase transition is expected to occur. In short, this can be explained by noting that chains cannot form isotropic aggregates, and therefore the spatial correlation cannot diverge. However, Monte Carlo simulations of DHS have provided evidence of the existence of a LGT critical point at low temperature and density [5].

---

2We follow the derivation in [4].
We start by using a coarse-grained description of DHS as polymer-chains. At nonzero temperatures the chaining process may present two types of defects: Y-Junctions (Fig. 4B and Fig. 4D) and chain ends. These defects have higher energy with respect to the perfect chain. If we consider the defects to behave like an Ideal Gas, we have

$$ f = k_B T \rho (\ln \rho - 1) + \rho \epsilon, $$

(12)

where $\epsilon$ and $\rho$ are the energy cost and concentration of the defect. Minimizing with respect to the concentration we get that optimal concentration is $\rho^* = e^{-\epsilon/K_B T}$ and the optimal free energy is $f^* = k_B T \rho^*$. Hence, The mean-field free energy, in units of $k_B T$, is given by

$$ f = -\rho_1 - \rho_3 + \frac{1}{2} \phi^2, $$

(13)

where the subscripts 1 and 3 represents chain ends and Y-Junctions, respectively. The Third Term is a mean-field term that accounts for the excluded volume of the HSs (see for instance section 4.3 of [1]).

Even though the $r^{-3}$ interaction is long-range the chain energy has a limit $-2u_d \sum_{n=1}^{\infty} 1/n^3 \simeq -2u_d (1.202)$, which means that only $\sim 20\%$ of the interaction energy is long-range and allows us to treat the interaction as shortranged. According to a mean-field analysis of polymer chains, we should have that $\phi \sim \psi^2(\vec{r})$, where $\psi(\vec{r})$ is the probability that a polymer chain ends at $\vec{r}$ (see for instance chapter IX of [6]). This can be understood by the fact that a chain site can be seen as the convergence of two chain ends. Similarly, we should have $\rho_1 \sim \psi$ and $\rho_3 \sim \psi^3$ which are the convergence of 1 and 3 chain ends, respectively. Adding boltzmann factors to account for the energy cost of the defects, we get

$$ \rho_1 \sim \psi e^{-\epsilon_1/T^*} \sim \phi^{1/2} e^{-\epsilon_1/T^*}, $$

(14a)

$$ \rho_3 \sim \psi^3 e^{-\epsilon_3/T^*} \sim \phi^{3/2} e^{-\epsilon_3/T^*}. $$

(14b)

Therefore, Eq. 13 becomes

$$ f = -(2\phi)^{1/2} e^{-\epsilon_1/T^*} - \frac{1}{3} (2\phi)^{3/2} e^{-\epsilon_3/T^*} + \frac{1}{2} \phi^2. $$

(15)

The pressure is given by

$$ p = \phi^2 \frac{\partial}{\partial \phi} \left( \frac{f}{\phi} \right) = \frac{1}{2} \left( \phi^2 + \rho_1 - \rho_3 \right). $$

(16)

where we see that there is an attraction, due to the Y-Junctions, and a repulsion, due to the chain ends. Hence, there is a Y-Junction rich region which is energetically favorable, while a chain-end rich region which is entropically favorable, due to entropy contribution of the excluded volume (The aggregation of the Y-Junctions lowers the entropy). This competition leads to phase separation. Equating to zero the first and second derivatives of the pressure with respect to the density, we find the critical point

$$ T_c = \frac{\epsilon_1 - 3\epsilon_3}{3 \ln 3 - 2 \ln 2}, $$

(17a)

$$ \ln \phi_c = -\frac{\epsilon_1 (2 \ln 3 - \ln 2) - \epsilon_3 \ln 2}{\epsilon_1 - 3\epsilon_3}. $$

(17b)

In particular, we have that $\rho_1 = \rho_3$ at the critical point. Hence, that the transition is between a connected liquid phase ($\rho_1 < \rho_3$), with more junctions than ends, and a
disconnected gas phase ($\rho_1 > \rho_3$) as shown in Fig. 5. Thus, we see that, even though the DHSs do not form isotropic aggregates, the defects are capable of doing so and phase separating. This process is analogous to the demixing of a binary mixture.

The critical values found in [5] were $\rho_c \approx 0.05 - 0.07$ and $T^*_c \approx 0.15 - 0.16$. This gives $\epsilon_1 \approx 0.67$ and $\epsilon_3 \approx 0.12$. Using those values, we can compute the coexistence curve by performing Maxwell's construction. The phase diagram is shown in Fig. 5. The spinodal curve, defined as the points such that $\partial^2 f / \partial \phi^2 = 0$, and the connectivity line, defined as the points such that $\rho_1 = \rho_3$, are also shown. Note that, as the temperature is lowered both the gas and liquid densities approach zero exponentially and the coexistence regions vanishes at $T = 0$, where the systems exhibits perfect chaining. This result should be compared to the typical parabolic shape shown in the previously studied demixing.

In a successive work [7], they argued that, if $\epsilon_3 < \epsilon_1 / 3$, the energy cost of forming a junction cannot overcome its entropy gain and the critical point does not exist (details not shown here). The correct values of $\epsilon_1$ and $\epsilon_3$ are hard to predict, however most energy values in the estimated range obey this rule.

### 4 Patchy Particles

We consider a system of $N$ HSs of radius $\sigma$ and volume $v_s = \pi \sigma^3 / 6$ each with valence $M$, that is, with $M$ interaction sites. One of the simplest models of patchy particles is the Kern-Frenkel potential [8]. In this model, a patchy particle consists of a HS with binding sites at its surface. The interaction between two binding sites $\alpha$, at particle $i$, and $\beta$, at particle $j \neq i$, is given by $V_{ij,\alpha\beta} = V_{a\beta}^{SW}(r_{ij}) \times G(\hat{r}_{ij}, \hat{r}_{ij}, \hat{r}_{ij})$, where

![Figure 5: Phase Diagram of DHS. The full line is the Coexistence Curve, the dashed curve is the Spinodal Curve and the dotted line is the connectivity curve. The three lines meet in the critical point. Extracted from [4].](image)
$V_{αβ}^{SW}(r_{ij})$ is the square-well potential, 

$$V_{αβ}^{SW}(r) = \begin{cases} 
\infty & r < σ, \\
-ϵ_{αβ} & σ < r < σ + δ_{αβ}, \\
0 & \text{otherwise}, 
\end{cases} \quad (18)$$

and $G$ is the angular dependency, 

$$G(\hat{r}_{ij}, \hat{r}_{ij}, \hat{r}_{ij}) = \begin{cases} 
1 & \hat{r}_{ij} \cdot \hat{r}_{iα} > \cos θ_{αβ}^\text{max} \text{ and } -\hat{r}_{ij} \cdot \hat{r}_{iβ} > \cos θ_{αβ}^\text{max} \\
0 & \text{otherwise}. 
\end{cases} \quad (19)$$

where $\hat{r}_{ij}$ is the distance between particles $i$ and $j$, $\hat{r}_{iα}$ and $\hat{r}_{iβ}$ are the distances (of length $σ/2$) between the particles and their respective binding sites. Futhermore, $ϵ_{αβ}$ is the energy interaction between the binding sites and $δ_{αβ}$ and $θ_{αβ}$ are the angular and radial ranges, respectively, which control the bonding volume, the volume of the configuration space available for bonding. Hence, the interaction between two particles is given by 

$$V_{ij} = \sum_{α ∈ Γ} \sum_{β ∈ Γ} V_{ij, αβ}, \quad (20)$$

where $Γ$ is the set of different binding sites of a given particle.

We assume that each binding site can only take part in one bond and every two spheres cannot interact by more than one bond. In this case, the free energy of the model can be computed quite accurately by the Wertheim Theory of associating fluids [9],[10]. This mean-field is based on a microscopic description of the patchy particles. It describes the patchy particles potential as a perturbation over the HS potential, for which a virtually exact free energy expression is known [12].

The derivation is quite involved and out of scope of the course, therefore, we only present the result as in [11]. The free energy (per particle) is given by 

$$βf = βf_{HS} + βf_{bond}, \quad (21)$$

where $f_{HS}$ is the Hard-Sphere free energy and 

$$βf_{bond} = \sum_{α ∈ Γ} \left( \ln X_α - \frac{X_α}{2} \right) + \frac{1}{2} M, \quad (22)$$

where $X_α$ is the fraction of molecules not bonded at site $α$. The $X_α$ are given by 

$$X_α = \frac{1}{1 + \sum_{β ∈ Γ} \rho X_β Δ_{αβ}}, \quad (23)$$

where $ρ$ is the total density and 

$$Δ_{αβ} = \int_{v_{ij}} g_{HS}(\vec{r}) \left[ \exp(βϵ_{αβ}) - 1 \right] d\vec{r}, \quad (24)$$

where $g_{HS}$ is the HS pair correlation function. There integral is calculated over the bonding volume $v_{ij}$. Note that different patchy particle models will have the same free energy as long as they have the same $Δ_{αβ}$. After solving for $βf$, the critical point can be found by setting to zero the first and second derivatives of the pressure with respect to the density, the spinodal curve can be found by setting to zero the second
derivative of $f$ with respect to the density and the coexistence curve can be found by performing Maxwell’s construction. Those procedures must be done numerically.

In [13] a similar patchy particle model has been studied using Wertheim’s Theory for patchy particles with only one type of binding sites ($\epsilon_{\alpha\beta} = \epsilon$) but different values of $M$ (see Fig. 6). Fractional values of $M$ were achieved by mixing particles with $M = 2$ and $M = 3$\footnote{The mean-field equations can be written analogously for two types of particles}. The range parameters where chosen such that two particles can form maximum one bond and binding sites cannot bind more than one binding site, as requested. The spinodal curves are shown in Fig. 7. Notice that as $M \to 2$ density approaches zero and for $M \leq 2$ the critical point disappears. This can be understood by the fact that, if $M = 2$ particles can only form chains, which is a one-dimensional process, and for $M = 1$ particles can only form dimmers, therefore the spatial correlation cannot diverge because most particles will be uncorrelated. The critical density seemed to be independent of the range, but the critical temperature was not.

In [14] a system of patchy particles with two Type A binding site and one type B binding sites was studied using Wertheim’s Theory. The relevant parameters in this problem where the bonding energies $\epsilon_{AA}$, $\epsilon_{BB}$ and $\epsilon_{AB}$. If $\epsilon_{BB}, \epsilon_{AA} >> \epsilon_{AB}$, the system will form perfect chains at $T = 0$, with X-Junction, (see Fig. 8(a)) and a critical point exists. This can be understood by defining an average binding $\langle f \rangle$, in analogy to the valence $M$. At $T=0$, $\langle f \rangle > 2$ and, therefore, the system is capable of forming isotropic aggregates at low temperatures. However, If $\epsilon_{BB} = 0$, X-Junctions

Figure 6: Patchy particles with different valence $M$. Extracted from [13].

Figure 7: Spinodal Curves of patchy particles with different average valence $\langle M \rangle$. Extracted from [13].
are forbidden and $\langle f \rangle = 2$ at $T = 0$. Nevertheless, for $T > 0$, the system may form chain ends and, if $\epsilon_{AB} > 0$, Y-junctions (see Fig. 8). Thus, the competition between chain ends and Y-Junctions may allow the existence of a critical point.

In such case, A parallel between the patchy particles and DHS can be made by setting $2\epsilon_1 = \epsilon_{AA}$ (since two ends are formed when one AA-bond is broken) and $\epsilon_3 = -\epsilon_{AB} + \epsilon_{AA}/2$ (since when a junction is formed, an end and an AB-bond are created). It was shown that there is a critical point for $\epsilon_{AB} > \epsilon_{AA}/3$. This is analogous to the condition $\epsilon_3 < \epsilon_1/3$. Moreover, it was also explained that if $\epsilon_{AB} > \epsilon_{AA}/2$, it is preferable to break a chain (losing $2\epsilon_{AA}$) and form Y-Junctions (gaining $\epsilon_{AB}$) and, therefore, at $T = 0$, $\langle f \rangle > 2$ and the usual LGT is recovered. This can be compared to the condition $\epsilon_3 > 0$. Hence, for $\epsilon_{AA}/3 < \epsilon_{AB} < \epsilon_{AA}/2$, it is expected have the LGT of DHS.

In [15], patchy particles with two binding sites of type A on the poles and nine binding of type B on the equator were investigated. Following [14], it was chosen $\epsilon_{BB} = 0$ and $\epsilon_{AA}/3 < \epsilon_{AB} < \epsilon_{AA}/2$. The phase diagram computed using Wertheim’s is shown in Fig. 9 as well as the phase diagram computed with Monte Carlo Simulations. The pinched shaped phase diagram was also found, showing that the two systems have extremely similar properties indeed. This parallel was explored in [15] to explain the some properties of the behaviour of the phase transition of DHS based on results of patchy particles.

---

4At $T = 0$, Y-junctions will form until all B-sites are bonded with A-sites and the remaining unbonded A-sites can still form bonds between each other. Therefore, all site will be bonded, except for sterical effects.
Figure 9: Coexistence curves of the model. (a) Numerical MC data. (b) Theoretical predictions. Extracted from [15].

5 Conclusion

We have shown evidence that, due to a competition between defects, DHS will exhibit a critical point or not, depending on the energy cost of forming junctions. Nevertheless, unlike the LGT in isotropic liquids, the critical temperature and density are quite low and the coexistence region vanishes as $T \to 0$ due to chaining between the dipoles. Moreover, We have seen that the phase diagram of DHSs will have a pinched shape and that we can build models that exhibit similar phase diagrams based on the competition between topological defects. In particular, the patchy particle model proposed in [15] has a strong parallel with DHSs, and their properties can be inferred by investigating such model.

Understanding the LGT of DHS is a very interesting problem and it may give insight into the LGT of molecules with more complex directional interactions such as H$_2$O and NH$_3$. An interesting question that I believe is not answered yet is whether the DHS critical point belongs to the same dimensionality class as the critical point of the a typical LGT with parabolic shape.

The Mean-Field analysis done in [4] required great physical intuition of the problem and it was the most remarkable step shown here. Another important aspect is the role of Self-Assembly in phase separation, in whether the LGT occurs and in what shape does the phase diagram has. To understand such aspects, Patchy particles seem to be a prominent tool and I believe that they will be the building blocks of different self-assembling colloids. Furthermore, their synthesis and numerical simulations are getting closer and closer, which means that numerical and theoretical findings will be easier to be tested and implemented experimentally.

References


