Phase diagram of patchy colloids: towards empty liquids

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We report theoretical and numerical evaluations of the phase diagram for patchy colloidal particles of new generation. We show that the reduction of the number of bonded nearest neighbours offers the possibility of generating liquid states (i.e. states with temperature $T$ lower than the liquid-gas critical temperature) with a vanishing occupied packing fraction ($\phi$), a case which can not be realized with spherically interacting particles. Theoretical results suggest that such reduction is accompanied by an increase of the region of stability of the liquid phase in the ($T$-$\phi$) plane, possibly favoring the establishment of homogeneous disordered materials at small $\phi$, i.e. stable equilibrium gels.

The physico-chemical manipulation of colloidal particles is growing at an incredible pace. The large freedom in the control of the inter-particle potential has made it possible to design colloidal particles which significantly extend the possibilities offered by atomic systems.

An impressive step further is offered by the newly developed techniques to assemble (and produce with significant yield) colloidal molecules, particles decorated on their surface by a predefined number of attractive sticky spots, i.e. particles with specifically designed shapes and interaction sites. These new particles, thanks to the specificity of the built-in interactions, will be able not only to reproduce molecular systems on the nano and micro scale, but will also show novel collective behaviors. To guide future applications of patchy colloids, to help designing bottom-up strategies in self-assembly and to tackle the issue of interplay between dynamic arrest and crystallisation — a hot-topic related for example to the possibility of nucleating a colloidal diamond crystal structure for photonic applications — it is crucial to be able to predict the region in the ($T$-$\phi$) plane in which clustering, phase separation or even gelation is expected.

While design and production of patchy colloids is present-day research, unexpectedly theoretical studies of the physical properties of these systems have a longer history, starting in the eighties in the context of the physics of associated liquids and to the specificity of the built-in interactions, will be able not only to reproduce molecular systems on the nano and micro scale, but will also show novel collective behaviors. To guide future applications of patchy colloids, to help designing bottom-up strategies in self-assembly and to tackle the issue of interplay between dynamic arrest and crystallisation — a hot-topic related for example to the possibility of nucleating a colloidal diamond crystal structure for photonic applications — it is crucial to be able to predict the region in the ($T$-$\phi$) plane in which clustering, phase separation or even gelation is expected.

While design and production of patchy colloids is present-day research, unexpectedly theoretical studies of the physical properties of these systems have a longer history, starting in the eighties in the context of the physics of associated liquids and interaction sites.

We present results of extensive numerical simulations of this model in the grand-canonical ensemble to evaluate the location of the critical point of the system in the ($T$-$\phi$) plane as a function of $M$. We complement the simulation results with the evaluation of the region of thermodynamic instability according to the Wertheim theory. Both theory and simulation confirm that, on decreasing the number of sticky sites, the critical point moves toward smaller $\phi$ and $T$ values. We note that while adding to hard-spheres a spherically symmetric attraction creates a liquid-gas critical point which shifts toward larger $\phi$ on decreasing the range of interaction, the opposite trend is presented here when the number of interacting sites is decreased. Simulation and theory also provide evidence that for binary mixtures of particles with two and three sticky spots (where $M$), the average $M$ per particles, can be varied continuously down to two patches number.

In this Letter we study a system of hard-sphere particles with a small number $M$ of identical short-ranged square-well attraction sites per particle (sticky spots), distributed on the surface with the same geometry as the recently produced patchy colloidal particles.

We identify the number of possible bonds per particle as the key parameter controlling the location of the critical point, as opposed to the fraction of surface covered by attractive patches. We present results of extensive numerical simulations of this model in the grand-canonical ensemble to evaluate the location of the critical point of the system in the ($T$-$\phi$) plane as a function of $M$. We complement the simulation results with the evaluation of the region of thermodynamic instability according to the Wertheim theory. Both theory and simulation confirm that, on decreasing the number of sticky sites, the critical point moves toward smaller $\phi$ and $T$ values. We note that while adding to hard-spheres a spherically symmetric attraction creates a liquid-gas critical point which shifts toward larger $\phi$ on decreasing the range of interaction, the opposite trend is presented here when the number of interacting sites is decreased. Simulation and theory also provide evidence that for binary mixtures of particles with two and three sticky spots (where $M$), the average $M$ per particles, can be varied continuously down to two patches number.

FIG. 1: Schematic representation of the location of the square-well interaction sites (centers of the small spheres) on the surface of the hard-core particle. Sticks between different interaction sites are drawn only to help visualizing the geometry.
by changing the relative concentration of the two species) the critical point shifts continuously toward vanishing $\phi$. This makes it possible to realize equilibrium liquid states with arbitrary small $\phi$ (empty liquids), a case which can not be realized via spherical potentials.

We focus on a system of hard-sphere particles (of diameter $\sigma$, the unit of length) whose surface is decorated by $M$ sites (see Fig. 1), which we collectively label $\Gamma$. The interaction $V(1, 2)$ between particles 1 and 2 is

$$ V(1, 2) = V_{HS}(r_{12}) + \sum_{AB} \sum_{BrT} V_{W}^{AB}(r_{AB}) \quad (1) $$

where the individual sites are denoted by capital letters, $V_{HS}$ is the hard-sphere potential, $V_{W}^{AB}(x)$ is a well interaction (of depth $-u_0$ for $x \leq \delta$, 0 otherwise) and $r_{12}$ and $r_{AB}$ are respectively the vectors joining the particle-site and the site-site centers [20]. Geometric considerations for a three touching spheres configuration show that the choice $\delta = 0.5(\sqrt{5} - 2\sqrt{3} - 1) \approx 0.119$ guarantees that each site is engaged at most in one bond. With this choice of $\delta$, $M$ is also the maximum number of bonds per particle. Temperature is measured in units of $u_0$ (i.e. Boltzmann constant $k_B = 1$).

To locate the critical point, we perform grand-canonical Monte Carlo (GCMC) simulations and histogram re-weighting [21] for $M = 5$, 4 and 3 and for binary mixtures of particles with $M = 3$ (fraction $\alpha$) and $M = 2$ (fraction 1 - $\alpha$) at five different compositions, down to $\langle M \rangle = 3\alpha + 2(1 - \alpha) = 2.43$. We implement MC steps composed each by 500 random attempts to rotate and translate a random particle and one attempt to insert or delete a particle. On decreasing $\langle M \rangle$, numerical simulations become particularly time-consuming, since the probability of breaking a bond $\sim e^{1/T}$ becomes progressively small. To improve statistics, we average over 15-20 independent MC realizations. Each of the simulations lasts more than $10^6$ MC steps. After choosing the box size, the $T$ and the chemical potential $\mu$ of the particle(s), the GCMC simulation evolves the system toward the corresponding equilibrium density. If $T$ and $\mu$ correspond to the critical point values, the number of particles $N$ and the potential energy $E$ of the simulated system show ample fluctuations between two different values. The linear combination $x \sim N + sE$ (where $s$ is named field mixing parameter) plays the role of order parameter of the transition. At the critical point, its fluctuations are found to follow a known universal distribution, i.e. (apart from a scaling factor) the same that characterises the fluctuation of the magnetisation in the Ising model [21]. Recent applications of this method to soft matter can be found in Ref. [22, 23, 24].

Fig. 2 shows the resulting density fluctuations distribution $P(\phi)$ at the estimated critical temperature $T_c$ and critical chemical potential(s) $\mu_c$ for several $M$ values [22]. The distributions, whose average is the critical packing fraction $\phi_c$, shift to the left on decreasing $M$ and become more and more asymmetric, signalling the progressive increasing role of the mixing field. In the inset, the calculated fluctuations of $x$, $P(x)$, are compared with the expected fluctuations for systems in the Ising universality class [21] to provide evidence that (i) the critical point has been properly located; (ii) the transition belongs to the Ising universality class in all studied cases. The resulting critical parameters are reported in Table I. Data show a clear monotonic trend toward decreasing $T_c$ and $\phi_c$ on decreasing $M$.

Differently from the $\phi_c$-scale, which is essentially controlled by $M$, $T_c$ depends on the attractive well width. Experimentally, values of $u_0/k_BT$ comparable to the ones reported in Table I can be realized by modifying the physical properties (size, polarizability, charge, hydrophobicity) of the patches [3, 4, 5] or by functionalizing the surface of the particle with specific molecules [26, 27].

One interesting observation stemming from these results is that reduction of $M$ makes it possible to shift $\phi_c$ to values smaller that $\phi = 0.13$, which is the lowest $\phi_c$ possible for attractive spherical potentials. Indeed for spherical square well potentials $0.13 < \phi_c < 0.27$, the two limits being provided by the Van der Waals (in which repulsion is modelled by the Carnahan-Starling expression) and by the Baxter [22] models, respectively with infinite and infinitesimal interaction range. We also note that results are consistent with those based on a toy model where an ad-hoc constraint was added to limit valency [28] and also with previous studies of particles interacting with non-spherical potentials [29, 30].

Visual inspection of the configurations for small $\langle M \rangle$ shows that the system is composed by chains of two-coordinated particles providing a link between the three-coordinated particles, effectively re-normalizing the bonding distance between the $M = 3$ particles. On adding more $M = 2$ particles, the bonding distance between $M = 3$ particles increases, generating smaller and
Critical chemical potential (in units of \(\mu m\))

\[
\beta A_{\text{bond}} = \frac{1}{N} \sum_{\text{Act}} \left( \ln X_A - \frac{X_A}{2} \right) + \frac{1}{2} M. \tag{2}
\]

Here \(X_A\) is the fraction of sites A that are not bonded. The \(X_A\)s are obtained from the mass-action equation

\[
X_A = \frac{1}{1 + \sum_{\text{Act}} \rho X_B \Delta A_{AB}} \tag{3}
\]

where \(\rho = N/V\) is the total number density and \(\Delta A_{AB}\) is defined by

\[
\Delta A_{AB} = 4\pi \int g_{HS}(r_{12}) \langle f_{AB}(12) \rangle_{\omega_1, \omega_2} r_{12}^2 dr_{12}. \tag{4}
\]

Here \(g_{HS}(12)\) is the reference HS fluid pair correlation function, the Mayer \(f\)-function is \(f_{AB}(12) = \exp(-V_{AB}^1(r_{AB})/k_BT) - 1\), and \(\langle f_{AB}(r_{12}) \rangle_{\omega_1, \omega_2}\) represents an angular average over all orientations of molecules 1 and 2 at fixed relative distance \(r_{12}\).

The evaluation of \(\Delta A_{AB}\) requires an expression for \(g_{HS}(r_{12})\) in the range where bonding occurs. We have used the linear approximation \[12\]

\[
g_{HS}(r) = 1 - 0.5\phi + \frac{9}{2} \left(1 - \phi^2\right)^2 (r - 1) \tag{5}
\]

which provides the correct Carnahan-Starling \[34\] value at contact.

To locate the critical point, we calculate the equation of state \(P(V,T) \equiv -\partial(A_{HS} + A_{\text{bond}})/\partial V_T\) and search for the \(T\) and \(\phi\) value at which both the first and the second volume (\(V\)) derivative of the pressure (\(P\)) along isotherms vanish. Fig. 3 shows a quantitative comparison of the numerical and theoretical estimates for the critical parameters \(T_c\) and \(\phi_c\). Theory predicts quite accurately \(T_c\), but slightly underestimates \(\phi_c\), nevertheless clearly confirms the \(M\) dependence of the two quantities. The overall agreement between Wertheim theory and simulations reinforces our confidence in the theoretical predictions and supports the possibility that on further decreasing \(\langle M\rangle\), a critical point at vanishing \(\phi\) can be generated.

TPT allows us also to evaluate the locus of points where \(\partial P/\partial V_T = 0\), which provide (at mean field level) the spinodal locus. The predicted spinodal lines in the \((T - \phi)\) plane for several \(M\) values are shown in Fig. 4. On decreasing \(M\) also the liquid spinodal boundary moves to lower \(\phi\) values, suggesting that the region of stability of the liquid phase is progressively enhanced. It will be desirable to investigate the structural and dynamical properties of such empty liquids by experimental and numerical work on patchy colloidal particles.

We note that our predictions are relevant to a larger class of functionalized particles, when particle-particle interaction is selective and limited in number. Very new
The square well interaction, among all short-ranged potentials, provides a sharp definition of bonding, avoids multiple bonding (choosing the appropriate $\delta$) and allows for a close comparison with the Wertheim theory.

For particles interacting with attractive spherical potentials, phase separation always destabilises the formation of a homogeneous arrested system at low $T$. Instead, it is foreseeable that, with small $\langle M \rangle$ patchy particles, disordered states in which particles are interconnected in a persistent gel network can be reached at low $T$ without encountering phase separation. Indeed at such low $T$, the bond-lifetime will become comparable to the experimental observation time. Under these conditions, a dynamic arrest phenomenon at small $\phi$ could take place. It would be possible to approach dynamic arrest continuously from equilibrium and to generate a state of matter as close as possible to an ideal gel [35].

We acknowledge support from MIUR-Firb, MIUR-Prin and MCRTN-CT-2003-504712. We thank K. Binder, D. Frenkel and J. Horbach for helpful discussions.

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25. Close to the critical point, the correlation length of the system can be reached at low $M$.
26. Decreasing $M$.
27. The study of the structural and dynamic properties of these low $M$ equilibrium systems will hopefully help developing a unified picture of other interesting network formation phenomena taking place at low $\phi$.
28. For particles interacting with attractive spherical potentials, phase separation always destabilises the formation of a homogeneous arrested system at low $T$. Instead, it is foreseeable that, with small $\langle M \rangle$ patchy particles, disordered states in which particles are interconnected in a persistent gel network can be reached at low $T$ without encountering phase separation. Indeed at such low $T$, the bond-lifetime will become comparable to the experimental observation time. Under these conditions, a dynamic arrest phenomenon at small $\phi$ could take place. It would be possible to approach dynamic arrest continuously from equilibrium and to generate a state of matter as close as possible to an ideal gel.
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[0.05, 0.15] 0.15
FIG. 4: Spinodal curves calculated according to TPT for the studied patchy particles for several $M$ and $\langle M \rangle$ values.

materials belonging to this class are the recently synthesised DNA-coated particles [26]. In this case, $M$ can be varied by controlling the number of strands and the attractive strength can be reversibly tuned by varying the length of the strands. Ratios of $u_0/k_BT$ comparable to the ones discussed here can be realized. Again, the phase diagram of these new materials has not been experimentally measured yet and we hope our work will provide a guideline.