Association of limited valence patchy particles in two dimensions

Piero Tartaglia[1,2] **and Francesco Sciortino**[1,3]

[1] Dipartimento di Fisica, Università di Roma La Sapienza, Piazzale Aldo Moro 2,
I-00185 Rome, Italy
[2] CNR-INFM-SMC, Università di Roma La Sapienza, Piazzale Aldo Moro 2,
I-00185 Rome, Italy
[3] CNR-INFM-SOFT, Università di Roma La Sapienza, Piazzale Aldo Moro 2,
I-00185 Rome, Italy

Abstract
We investigate theoretically the phase behavior of particles with limited valence in two
dimensions, by solving the first-order Wertheim theory form. As previously found for three
dimensions, in two dimensions also the valence has a strong impact on the phase diagram,
controlling the location of the gas–liquid coexistence. On decreasing the valence, the critical
density and temperature decrease while the region of gas–liquid instability shrinks and
vanishes. At low temperatures, the system reaches its ground state with particles forming a fully
bonded network which spans the system.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

In recent years, there has been considerable interest in investigating the phase behavior (both ordered and disordered arrangements) of colloidal particles in two dimensions [1–5]. This investigation is facilitated both by the possibility of confining colloidal particles at interfaces [6], and by the often non-negligible role of gravity that forces particles to sediment at the bottom of the sample holder [7]. The possibility of imaging the location of the particles in a large space window allows for an accurate reconstruction of the structure of the colloidal two-dimensional state, providing an ideal reference system for numerical and theoretical modeling. Most of the work has been devoted to the determination of the possible crystal structures and to the investigation of disordered dense states, in order to provide a fully resolved (and visual) description of the onset of slow dynamics and glass formation.

Less effort has been expended in the direction of investigating two-dimensional low density states and the possibility of forming arrested states at low density, with mechanisms different from packing. In the three-dimensional case, a series of articles have shown that arrested states at low density—not mediated by a precursive phase separation process [8]—are possible if the valence of the interacting particles is limited to small numbers [9–11]. In other words, particles able to form only a limited number of attractive contacts with their neighbors are characterized by a gas–liquid instability. The latter becomes more and more suppressed (in temperature and density) on decreasing valence, opening a large window of densities where the system forms a network structure in which the bond lifetime becomes the leading element in controlling the dynamics. Support for this picture has been provided by theoretical studies based on the Wertheim theory [12, 13] and supported by accurate numerical investigations [14, 11, 15].

In this paper we generalize the Wertheim theory to patchy colloidal particles in two dimensions. Particles are able to form a limited number of bonds with their neighbors, via localized (or specific) interactions. We show that even in two dimensions, the width of the gas–liquid unstable region is controlled by the value of the valence, progressively shrinking and moving to vanishing temperatures and densities when the average valence approaches 2. As for the three-dimensional case, it should be thus possible to observe *equilibrium gels* [16, 17] in small-valence systems in two dimensions.

2. The model

We focus on a system of particles modeled as hard disks of diameter σ, whose circular contour is decorated by f bonding sites at fixed locations, the 2D version of the model previously

studied in 3D [10, 14]. Sites on different particles interact via a square-well potential. The interaction $V(\mathbf{1}, \mathbf{2})$ between particles **1** and **2** is

$$V(\mathbf{1}, \mathbf{2}) = V_{HD}(\mathbf{r_{12}}) + \sum_{i=1}^{f_i} \sum_{j=1}^{f_j} V_{SW}(\mathbf{r}_{12}^{ij}) \tag{1}$$

where the individual sites are denoted by i and j, V_{HD} is the hard-disk potential, $V_{SW}(x)$ is a square-well interaction (of depth $-u_0$ for $x \leqslant \delta\sigma$, 0 otherwise) and $\mathbf{r_{12}}$ and $\mathbf{r}_{12}^{ij}$ are respectively the vectors joining the particle centers and the site (on different particles) centers, with site i belonging to particle 1 and site j to particle 2.

For geometric reasons, if

$$\delta < \frac{\sqrt{5 - 2\sqrt{3}} - 1}{2} \approx 0.1196, \tag{2}$$

then each site is engaged at most in one bond. Hence, with this choice of δ, each particle can form only up to f bonds. Moreover, the hypothesis of sterical incompatibilities and *site blocking* assumed in the Wertheim theory are satisfied. We note that in this model bonding is properly defined: two particles are bonded when their pair interaction energy is $-u_0$. Distances are measured in units of σ. Temperature is measured in units of the potential depth u_0 (i.e. the Boltzmann constant $k_B = 1$) and, as usual, $\beta = 1/k_B T$.

3. The theory

The first-order thermodynamic perturbation Wertheim theory [12, 13, 18] provides an expression for the free energy of particles with a number f of attractive sticky sites on their surface, independently of the specific geometric arrangement of the sites. The theory assumes that all identical sites have the same probability of forming bonds and that the correlation between adjacent sites is missing. The fundamental assumption of the Wertheim theory is that the conditions of steric incompatibilities are satisfied: (i) no site can be engaged in more than one bond and (ii) no pair of particles can be double bonded. These steric incompatibilities are satisfied in the model thanks to the value of δ chosen for the short-ranged square-well attraction.

In the formulation of [19], the bond free energy density of a system of f-functional particles is

$$\frac{\beta F^{bond}}{S} = \rho \ln(1 - p_b)^f + \frac{1}{2} \rho f p_b \tag{3}$$

where S is the surface, $\rho = N/S$ is the particle number density and p_b is the bond probability. Since we assume equal reactivity for all sites, the bonding process can be seen as a chemical reaction between two unsaturated sites in equilibrium with a pair of bonded sites [20]. In this respect one can write

$$\frac{p_b}{(1 - p_b)^2} = \rho\sigma^2 e^{-\beta\mathcal{F}_b} \tag{4}$$

where $\mathcal{F}_b$ is the site–site bond free energy, i.e. the free energy difference between the bonded and the unbonded state.

The Wertheim theory predicts an expression for $\mathcal{F}_b$ in terms of liquid state correlation functions and spherically averaged Mayer functions. The Mayer factor averaged over the particle orientations (for a pair of sites) can be written as

$$\langle f(12) \rangle_{\omega_1, \omega_2} = (e^{\beta u_0 - 1}) \int_0^{2\pi} \frac{d\theta_1}{2\pi} \int_0^{2\pi} \frac{d\theta_2}{2\pi} \theta(\delta - r_{12}^{ij})$$
$$= (e^{\beta u_0 - 1}) S(x), \tag{5}$$

where the angles θ_1 and θ_2 identify the locations of the two active sites with respect to the line joining the centers of the particles. The double integral defining the function $S(x)$ can be partially performed and turns out to be

$$S(x) = \frac{1}{\pi^2} \int_{x - \frac{\delta(1+\delta)}{x}}^{1} du \, \arccos\left(\frac{0.5 - \delta^2 + x^2 - xu}{\sqrt{0.25 + x^2 - xu}}\right), \tag{6}$$

where $x = r_{12}/\sigma$ is the scaled distance.

According to Wertheim, $\beta\mathcal{F}_b$ can be written as

$$\sigma^2 e^{-\beta\mathcal{F}_b} = f\Delta, \tag{7}$$

where Δ—which refers to a single site–site interaction (since all bonding sites are identical)—is given by

$$\Delta = 2\pi\sigma^2 \int_1^{1+\delta/\sigma} (e^{\beta u_0} - 1) x g_{HD}(x) S(x) \, dx. \tag{8}$$

The two-dimensional radial distribution function $g_{HD}(x)$ has been evaluated using a model for hard disks proposed by Yuste and Santos [21]. The theory uses a scheme of interpolation between the hard rod and hard sphere Percus–Yevick radial distribution functions $g_{HD}(x)$, and it has been shown to provide an accurate modeling of the HD behavior in the region of densities of interest for the present work. To numerically solve equation (8), we have expanded to second order in x the Yuste and Santos [21] expression, in the x region $(1, 1 + \delta)$. The resulting η dependence of Δ—where $\eta = \pi\rho\sigma^2/4$ is the covered surface fraction—arising from the η dependence of the hard-disk radial distribution function is shown in figure 1. We note that for $\rho\sigma^2 < 0.05$, the ideal gas expression $g_{HD}(x) \approx 1$ can be confidently used. Finally, p_b is

$$p_b = 1 - \frac{2}{1 + \sqrt{1 + 4f\rho\sigma^2\Delta}}. \tag{9}$$

The pressure can be obtained by summing the hard-disk and the bonding contributions. The hard-disk pressure has been calculated as suggested in [22]:

$$P(v, T) = T\rho \frac{1 + (1 - 2a)\eta^2}{(1 - \eta)^2} \tag{10}$$

where the parameter a is given by

$$a = \frac{2\sqrt{3}}{\pi} - \frac{2}{3}. \tag{11}$$

The total pressure can be obtained by summing, to the HD contribution, the surface derivative of the bond free energy (equation (3)).
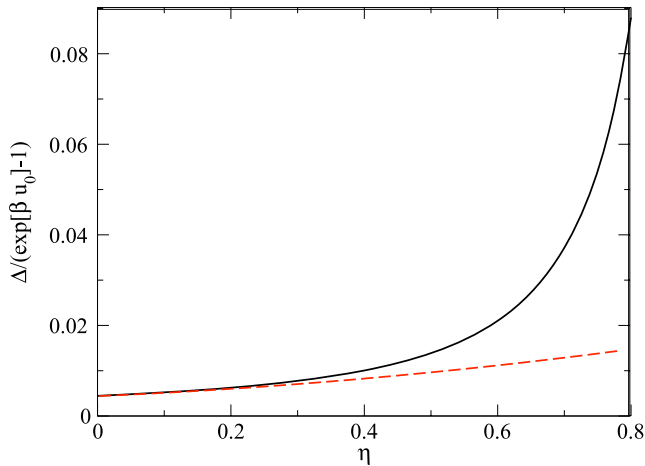
Figure 1. Dependence of the bonding surface $\Delta/(\exp[\beta u_0] - 1)$ versus η calculated according to equation (8) (full line) and the low η expansion (dashed line) $0.004\,372\,00 + 0.006\,421\,99\eta + 0.008\,105\,84\eta^2$. Assuming an ideal gas as reference system (instead of the hard-disk case) corresponds to selecting the $\eta = 0$ value for Δ.

4. Results

We start by evaluating the role of the valence in the phase diagram of the system, to confirm the behavior which has been observed in the three-dimensional case.

Figure 2(a) shows the phase diagrams for disks with various functionality f values, from 5 down to the binary mixture case of tri-functional and bi-functional particles with average functionality $f = 2.1$. For valence strictly equal to 2, the system forms chains and does not phase separate into a gas and a liquid phase at any finite T [23]. Figure 2(b) shows the corresponding P–T projection, clarifying that the critical pressure approaches zero on reducing the valence. For valence 5, the phase separation region encompasses the entire range of densities accessible to hard two-dimensional systems. Indeed, in 2D, random packing of disks in a disordered configuration can reach packing of the order of 0.84 [24]. Hence, according to the Wertheim theory, for valence 5 (or more, i.e. in the isotropic limit) the entire low T region is dominated by phase-separated states, and it is

impossible to generate arrested states at low densities without the intervention of a decomposition kinetics which creates locally high density regions. Such results are consistent with the expectations, since in two dimensions, the most packed local arrangements are characterized by six neighbors. In this respect, the five-patch case does not differ too much from a spherical potential case.

For smaller valences the case is different since the liquid branch of the coexistence curve progressively moves to smaller densities, opening up a wider and wider region of packing where a homogeneous liquid phase is found. Data clearly show that the region of gas–liquid phase separation is progressively reduced and shifted toward the left on decreasing the valence. If crystallization is avoided (kinetically or thermodynamically), then the liquid can exist in a stable or metastable state down to very small temperatures, where the lifetime of the bonds becomes so long that no bond-breaking processes are encountered in any finite observation time, and the system becomes non-ergodic. For very small average valences, the liquid branch has moved to very small density and at low T, arrested non-ergodic states can be found also for small densities. Hence, small-valence systems provide a case in which arrest can be progressively reached without the intervention of phase separation, even at small densities. Note that these arrested states are different from 'jammed' states in granular matter, or 'glass' states, where the motion of the particles is severely constrained to localization lengths significantly smaller than the particle size.

Figure 2(a) also shows the percolation line evaluated according to the mean-field Flory–Stockmayer predictions, which has been shown to be based on the same assumptions as the Wertheim theory (i.e. closed loops of bonds are neglected) [11]. For particles with integer functionality, percolation is expected at $p_b^p = 1/(f - 1)$ [25], while for mixtures of tri-functional and bi-functional particles (with relative composition x_3 and x_2) it is expected at $p_b^p = 1/(1 + p_3)$, with $p_3 = 3x_3/(2x_2 + 3x_3)$. As in previously investigated cases, the percolation line is located above the gas–liquid coexistence region (so percolation is a prerequisite for phase separation [26]) and tends to become tangent to the low density spinodal when temperature approaches zero. The observed
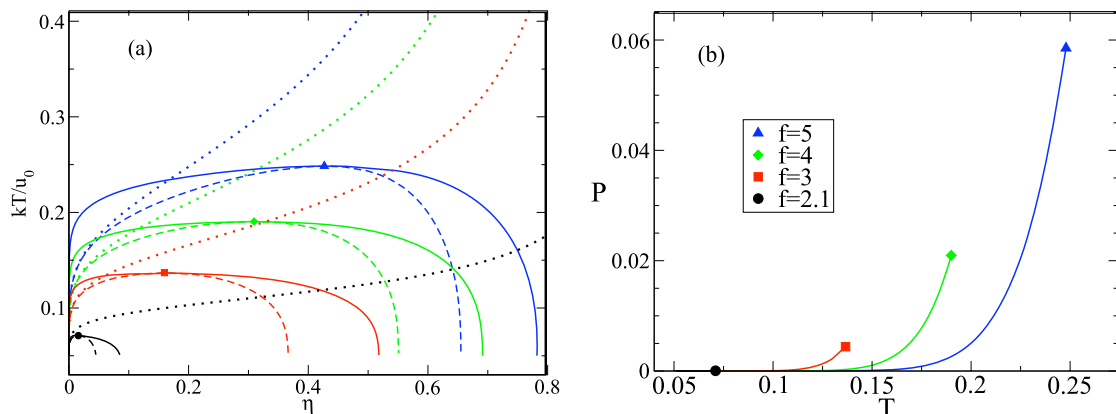

Figure 2. (a) The critical points, and the spinodal, binodal and percolation lines for various values of the (average) functionality $f = 5, 4, 3, 2.1$ from high to low temperatures. (b) The binodal lines and critical points for various values of f in the pressure–temperature plane.
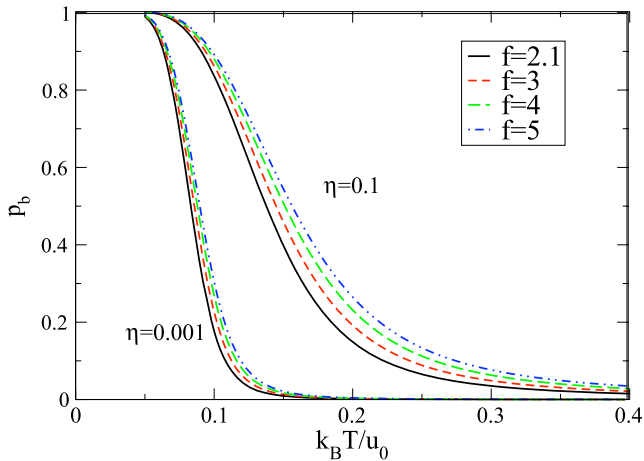
Figure 3. Bond probability p_b versus temperature for two different surface packings.

location of the percolation line confirms that in 2D also, the liquid state (defined as usual as all state points with T less than the critical temperature) is well inside the percolation region, where the fraction of particles in the infinite cluster has almost reached its asymptotic value of 1. This suggests that, in these patchy models, the liquid is composed of one infinite size cluster to which essentially all the particles are connected.

Figure 3 shows the T dependence of the probability of forming a bond p_b, for two different densities. The probability has a sigmoidal shape, converging to unity at small temperatures. Since the bond probability in this model is proportional to the number of bonds formed, and hence to the potential energy of the system, the sigmoidal shape indicates that in two dimensions also, a specific heat peak at constant V will be found, confirming that this feature can be considered a clear signature of an underlying bonding process. The approach to $p_b = 1$ at low T indicates that all the possible bonds that can be formed in the system are indeed saturated. The system essentially reaches its (disordered) ground state at a finite temperature. At these low temperatures, the bond lifetime, which can be reasonably estimated as $\sim \exp(-\beta u_0)$, becomes extremely long, conferring to the system the typical character of a dynamically arrested material. This suggests, in agreement with the three-dimensional case, that in these low valence systems, dynamic arrest is not connected to difficulties in the exploration of a complex landscape.

5. Conclusions

In this paper we have presented an application of the Wertheim theory to a two-dimensional assembly of patchy particles, modeled analogously to the previously investigated three-dimensional case. The theoretical results reproduce the effects which have been predicted and confirmed in simulations in 3D. The sensitivity of the phase diagram to the valence is confirmed, together with the possibility of forming, when the valence is small, equilibrium fully bonded structures (gels), the existence of a specific heat peak being the hallmark of the bond-driven assembly in the system. Hence, a two-dimensional system can provide an interesting case

for experimentally testing the possibility of creating empty liquids [10] and their structure.

The present results also call for a numerical verification of the quality of the Wertheim predictions in two dimensions and, in particular, the role of the loops of bonds in the self-assembly of these low valence systems. Indeed, it is well known that rings of bonds (analogous to the probability of return to the origin of a random walker) are significantly enhanced in low dimensions. Simulations in this direction are under way, to estimate the significance of the bond loops at low dimensions as well as the dynamic properties of the two-dimensional gel, in both limits of finite and infinite lifetimes of the bonds.

Acknowledgments

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