Attraction-driven disorder in a hard-core colloidal monolayer

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Monte Carlo simulation techniques were employed to explore the effect of short-range attraction on the orientational ordering in a two-dimensional assembly of monodisperse spherical particles. We find that if the range of square-well attraction is approximately 15% of the particle diameter, the dense attractive fluid shows the same ordering behavior as the same density fluid composed of purely repulsive hard spheres. Fluids with an attraction range larger than 15% show an enhanced tendency to crystallization, while disorder occurs for fluids with an attractive range shorter than 15% of the particle diameter. A possible link with the existence of ''repulsive'' and ''attractive'' states in dense colloidal systems is discussed. © *2004 American Institute of Physics.*
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I. INTRODUCTION

During the past few decades, systems composed of hard-core particles (platelets, spheres, rods) have been the subject of continuous and intense research.[1–6] Such stable interest is a recognition of an outstanding role played by hard-core models in many different areas of applied and basic science, including nanostructured and granular materials,[1,2] fundamental problems of self-organization and phase transitions,[3,4] random close packing,[5] etc. One of the earliest applications of hard-core (HC) particles concerns colloids.[6] Recently, there has been renewed interest to a hard-core modeling of colloidal matter due to the peculiar sensitivity of the suspension's coexistence properties to the range of effective attraction experienced by colloid particles when a nonadsorbing polymer is added.[7–9] The range of this attraction is associated with the radius of gyration of the polymer and, in practice, can be varied by changing the size of the polymer. If the range of attraction is comparatively long, with respect to the colloid particle core diameter (σ), a colloidal substance can exist[6] in gaseous, liquid, and solid phases, analogous to an atomic substance, although a system of purely repulsive HC colloids does not show the liquid phase. As the range of induced attraction between particles decreases, the suspension's triple point is approached and, when the attraction range becomes less than about 30% of σ, the colloidal liquid phase disappears, and again, similarly to purely repulsive HC colloids, only a stable fluid phase remains in attractive colloids.[7] The question is as follows: how different are these ''repulsive'' (no polymer added) and ''attractive'' (with short polymer added) equilibrium colloidal fluids? Since when compressed, both repulsive and attractive colloidal fluids undergo a transition, first to a metastable (glassy) colloid phase and then to a stable colloid crystal phase, the answer to the question could be vital in understanding the nature of the ''repulsive'' and ''attractive'' glassy and solid states in a dense colloidal matter.[10,11]

To tackle this question, we performed a computer simulation study of equilibrium-fluid states in dense colloidal systems just before the transition to a metastable-fluid state. To mimic the colloid/polymer mixture, a HC model with an effective square-well (SW) attraction was used. In particular, we explored the effects of the range of SW interparticle attraction on the particle coordination and ordering in a two-dimensional (2-D) colloidal fluid. We have restricted the present study to a 2-D model, not only because of reasons of simplicity and easier visualization. Besides the fundamental importance (character of the melting transition, etc.), the 2-D model is equivalent, in some sense, to a monolayer of spherical particles, and in such a way is directly related to issues of practical importance that include the existence of adsorbed monolayers of colloidal particles[12] and the formation of ordered or glassy surface phases[13] observed in 3-D colloidal suspensions under confinement.

So far, to the our the best of knowledge, it is believed that an equilibrium 2-D system of monodisperse spherical particles whose interaction has an attractive part, should posses a higher degree of order than a system with a purely repulsive interaction.[4] In this paper, we show that the results obtained for the SW model with a varying range of attraction are far from obvious. Starting with an attraction range of 30% of σ, we find that by turning on the attractive SW interaction, the degree of order in equilibrium fluid is improved compared to what is observed for an unperturbed (purely repulsive) HC fluid of the same density. As the attraction well shrinks, the former effect becomes weaker and for an attraction range of approximately 15% of σ, the attractive SW fluid shows the same ordering behavior as the repulsive HC fluid. Reducing the SW attraction range further

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leads to the opposite trend: the turning on an attractive interaction results in a loss (melting) of particle coordination within the fluid monolayer formed by particles that are experiencing SW attraction in comparison to those with a purely repulsive HC interaction.

The remainder of this paper is organized as follows. The definitions of the model and properties that are calculated as well as the brief description of the simulation procedure are outlined in the following section. Section III contains our main results and a discussion of the conclusions that can be drawn from them. Finally, in Sec. IV we summarize the paper and outline some remarks and speculations.

II. BASIC DEFINITIONS AND SIMULATION DETAILS

To be specific, our study deals with a collection of N spherical particles of diameter σ spread into a monolayer of area S, with packing fraction $\phi = N\pi\sigma^2/4S$. Since the spheres are confined to move in a plane, we can treat the particles as hard disks. Then, to characterize the particle–particle interaction potential, we introduce the SW attraction which is superimposed on a HC repulsion as follows:

$$\begin{aligned} u(r) &= \infty, \quad r < \sigma, \\ &= -\epsilon, \quad \sigma \leqslant r < \sigma + \delta, \\ &= 0, \quad r \geqslant \sigma + \delta, \end{aligned} \tag{1}$$

where ϵ denotes the attractive well depth, and δ its width, i.e., the characteristic attraction ring outside the repulsive core σ. Without loss of generality, we assume $\sigma = 1$ in the remainder of the text. We have carried out a series of canonical and grand canonical Monte Carlo computer simulations for purely repulsive HC disks, i.e., assuming $\epsilon = 0$, $\delta = 0$ and for disks with an attractive interaction when $\epsilon \neq 0$ and $\delta \neq 0$. A square simulation cell with periodic boundary conditions and length side $L = 20$ for both ensembles was employed. The particles number N was varied from run to run to cover a range of values of the packing parameter ϕ. It is known that there is a pronounced system-size effect in the simulations of 2-D melting transition.[4] The use of a relatively modest system size in our study is justified by our primary interest in the prefreezing, i.e., equilibrium-fluid phase, and not in the transition region. Furthermore, we are interested in the qualitative changes of the ordering behavior in the systems composed of the same number of particles, i.e., the same size systems, but with different interaction parameters.

A standard Metropolis algorithm was applied to obtain the ensemble averages of the dense equilibrium fluid. The results from the simulation runs were equilibrated for at least 2×10^7 iterative steps. The productive runs were averaged at least over 600 configurations, each relaxed by 10^5 iterations. The acceptation rate was fixed between 20% and 30%.

Order within a monolayer formed from identical particles can take the form of translational and/or bond-orientational order. Translational order can be studied through the radial distribution function and is not an issue of the present study. A quantitative measure of bond-orientational (hexagonal) order is provided by the so-called ''global'' bond-orientational order parameter, ψ_6, that was evaluated during the simulation runs using the following definition:[5]

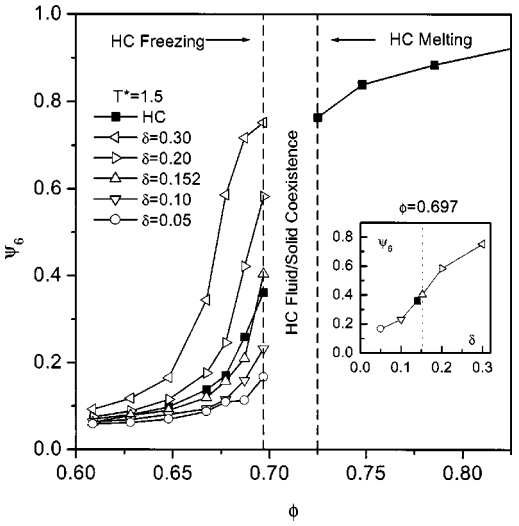

FIG. 1. Orientational order parameter ψ_6 versus packing fraction ϕ at a fixed attraction strength $T^* = 1.5$. Data correspond to the attractive SW fluid with several attraction ranges $\delta = 0.3$, 0.2, 0.152, 0.1, and 0.05, as indicated in the figure. For comparison, the data for a repulsive HC fluid are presented as well (filled symbols). Inset: ψ_6 versus attraction range δ at a fixed packing fraction $\phi = 0.697$; the notations are the same as on the main part of the figure. Lines are guides to the eye.

$$\psi_6 = \left| \frac{1}{N_{\mathrm{nn}}} \sum_{jk} e^{i6\theta_{jk}} \right|, \tag{2}$$

where j runs over all disks in the system, k runs over all ''geometric'' nearest neighbors (nn) of disk j, each obtained through the Voronoi analysis,[4] and N_{nn} is the total number of such nearest neighbors in the system. The angle θ_{jk} is defined between some fixed reference axis in the system and the vectors (''bonds'') connecting nearest neighbors j and k.

III. RESULTS AND DISCUSSION

Figure 1 displays the set of ψ_6 profiles versus particle packing ϕ for the HC and SW fluids. In the case of the HC fluid, which is the natural reference system in our study, the relationship between the orientational order and density seems to be well understood in the literature.[4] The data generated for a reference HC system in our study, displayed in Fig. 1, show that the fluid–solid transition in the repulsive HC fluid, as follows from our simulations, is similar to that found by other authors.[4] The latter may serve as a simple test of the computational procedure applied then to a system composed of particles with an attractive SW interaction as well as a test of a system size effect on the data collected for a SW fluid.

The main result of this letter follows from the analysis of the evolution of bond-orientational order parameter ψ_6 as we gradually change the range of the attractive interaction δ from $\delta = 0.3$ to 0.05. The attraction strength determined by the reduced parameter $T^* = kT/\epsilon$ in all cases remains fixed at $T^* = 1.5$. This value of T^* is well above the 2-D fluid–solid coexistence line,[9] i.e., the SW fluid is maintained in a prefreezing equilibrium-fluid state. As can be seen from Fig. 1, depending on the range of attraction δ, there are three different types of behavior of the orientational order parameter ψ_6^{SW} in an attractive SW fluid when compared to the orien-

tational order parameter ψ_6^{HC} of the reference HC fluid at the same packing fraction ϕ. First, turning on an attractive interaction with a range $\delta=0.3$ leads to a significant increase of orientational order in the SW fluid: ψ_6^{SW} in a prefreezing equilibrium-fluid phase exhibits a magnitude that is comparable to that of ψ_6^{HC} shown in a crystalline phase. Second, reducing the range of SW attraction (from $\delta=0.3$ to 0.2) causes ψ_6^{SW} to decline, and when the range of attraction is reduced to $\delta\approx0.15$, the orientational order in an attractive SW fluid practically follows the same scenario as the one observed for a reference HC fluid. Third, when δ is further reduced (from $\delta\approx0.15$ to 0.1 and 0.05), parameter ψ_6^{SW} continues to decrease, assuming values that are far lower than those observed for a purely repulsive counterpart, ψ_6^{HC}, at the same densities.

The inset of Fig. 1 presents the values assumed by the bond-orientational order parameter ψ_6 versus the range of attraction δ for the SW fluid at a fixed packing fraction $\phi=0.697$, that is just before the freezing point of the HC fluid, and corresponds to an equilibrium-fluid phase for an attractive SW fluid; the latter is ensured by the comparison with the phase diagram fluid simulated by Bolhuis *et al.*[9] The plot shows that the dense SW fluid with $\delta=0.3$ exhibits a very high degree of hexagonal ordering. However, as the range of induced attraction decreases, the SW fluid loses its ''global'' sixfold coordination, and when the attraction range becomes extremely short, $\delta=0.05$, the attractive SW fluid shows a very low ''global'' hexagonal order.

So far, we have analyzed the ordering phenomena in an attractive SW fluid with different attraction ranges δ, but at the same attraction strength T^*. Figure 2 shows ψ_6 vs ϕ at reduced temperatures $T^*=1$ (dashed lines) and $T^*=2$ (dotted lines) that are lower and higher, respectively, than $T^*=1.5$ discussed in Fig. 1 (shown by solid lines in Fig. 2). By decreasing the attraction strength (increasing the temperature), as expected, the SW fluid, irrespective of the range of the attraction, shows a tendency to approach the thermodynamic state of the unperturbed HC fluid. However, this occurs in two different ways (i) if $\delta>0.15$ ($\delta=0.3$ in Fig. 2), this is accompanied by a decrease of ψ_6, which is consistent with a melting of existing ordered domains, similar to what occurs in a simple (argonlike) fluid; (ii) if $\delta<0.15$ ($\delta=0.05$ in Fig. 2), this is accompanied by an increase of ψ_6, i.e., the SW fluid with a short-ranged attractive interaction becomes more ordered when the strength of attraction diminishes, in apparent contradiction with intuition. On the other hand, as the attraction strength increases, the orientational order parameter for the SW fluid, irrespective of the range of attraction, assumes the values that move away from the orientational order observed in the reference HC fluid. However, again it occurs in two different ways: (i) for a SW fluid with $\delta=0.3$, order parameter ψ_6 continues to grow, indicating a smooth expansion of the region with sixfold coordination to the lower densities; (ii) for a SW fluid with $\delta=0.05$, the quantitative changes in ψ_6 are not so apparent, although the tendency to low ordering persists.

The inset of Fig. 2 shows histograms of the fraction of particles that belong to five-, six- and sevenfold Voronoi polygons, at $\phi=0.697$ and $T^*=1$. One can clearly see the

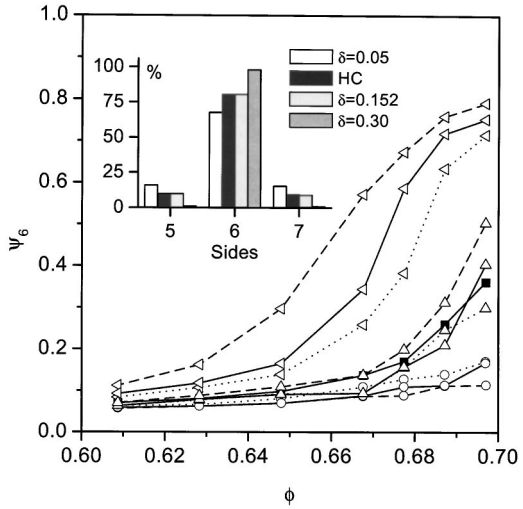

FIG. 2. The same as in Fig. 1, but at different attraction strengths for an attractive SW fluid: $T^*=1$ (dashed line), $T^*=1.5$ (solid line), and $T^*=2$ (dotted line). The three groups of curves correspond to the different attraction ranges: $\delta=0.3$, 0.152, and 0.05 with the same notations as in Fig. 1. Inset: fractions of the five-, six-, and seven-sided Voronoi polygons at packing fraction $\phi=0.697$ and attraction strength $T^*=1$. Lines are guides to the eye.

qualitative difference in the particle coordination within monolayers formed from the SW fluid with an attraction range that is larger ($\delta=0.3$), and shorter ($\delta=0.05$) than the crossover range $\delta\approx0.15$. If the attraction range is larger, almost all of the polygons are already hexagons, i.e., nearly all particles are six-coordinated, and the number of defects (particles not having six neighbors) is very small. In contrast, in a monolayer formed from a SW fluid with a shorter attraction range, about 30% of the particles are involved into odd-fold (pentagon and heptagon) configurations. The reference fluid of purely repulsive HC particles and SW fluid with $\delta=0.152$ are practically identical, both having about 20% of the particles that belong to defects.

The corresponding sequences of the defect maps and the individual particle trajectories, for the conditions discussed in the previous paragraph, are shown in Fig. 3. A structural analysis reveals that the monolayer formed from the SW fluid with $\delta=0.3$ is a nearly defect free and crystalline domains are already present; very few defects occur in the form of isolated or closely bound pairs. As the attraction range is reduced, the defect structure becomes more complicated involving chains for $\delta=0.15$, and grain boundaries and defect clusters for $\delta=0.05$. What we observe is a result of an increased particle motion due to the greater free volume in the system[14] when the attraction range becomes shorter. However, in the first stage, when the range is reduced from $\delta=0.3$ to 0.15, the particle motion is preferentially vibrational inside hexagonal cages (spots and chains on the trajectory plot are rather thick). When the range is further reduced from $\delta=0.15$ to 0.05, the traces of one-dimensional stringlike and rotational collective particle motion appear.[15]

IV. SUMMARY AND OUTLOOK

Summarizing, we presented here the results of MC simulations of the ordering behavior within a monolayer of

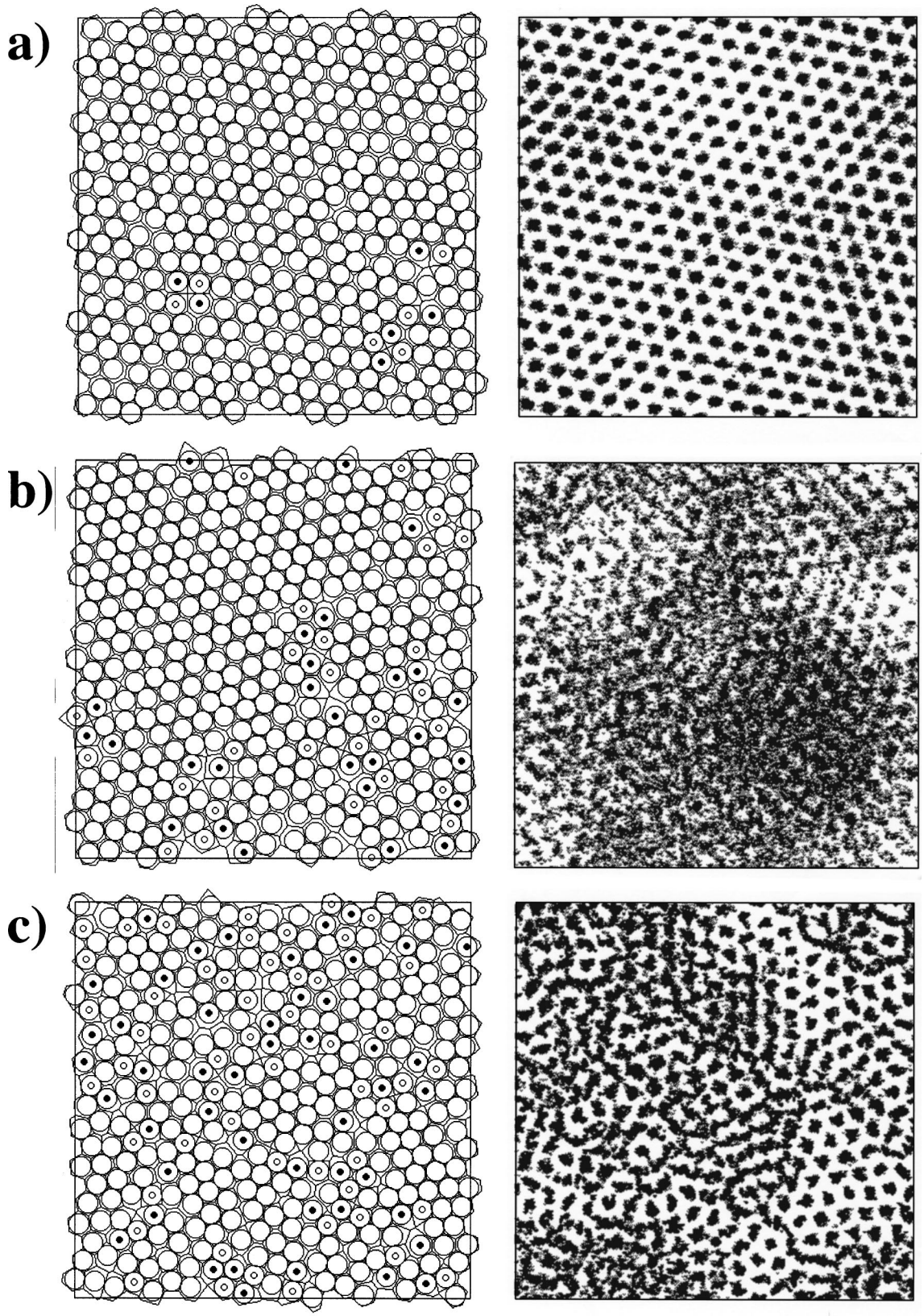

FIG. 3. The Voronoi analysis (left) and trajectory plots (right) obtained with the MC algorithm for 1000 consecutive iterations before equilibration, for an attractive SW fluid with different attraction ranges: $\delta=0.3$ (a), 0.152 (b), and 0.05 (c). All data correspond to packing fraction $\phi=0.697$ and attraction strength $T^*=1$. The empty circules represent particles with a hexagon arrangement, while circules with solid and hollow dots correspond to partcicles surrounded by five- and seven-sided Voronoi polygons, respectively. The data for a repulsive HC fluid are practically identical to that for $\delta=0.152$ (b).

spherical particles interacting via an attractive SW potential with an attraction range δ varying from 0.3 to 0.05. All simulations have been performed at the densities that correspond to the equilibrium-fluid phase, i.e., at the densities lower than freezing density. To quantify the order within the monolayer, the ''global'' bond-orientational parameter ψ_6 was evaluated during simulation runs. We find that if the range of square-well attraction is approximately 15% of the particle diameter,

the dense attractive fluid shows the same ordering behavior as the same density fluid composed of purely repulsive hard spheres. Fluids with an attraction range larger than 15% show an enhanced tendency to crystallization, while disorder occurs for fluids with an attractive range shorter than 15% of the particle diameter.

It is worthwhile to mention that the same density reference HC fluid with no attraction does not represent the limiting case $\delta \to 0$, but marks a crossover between two classes of attractive SW fluids that clearly is demonstrated by the data presented in the inset of Fig. 2. One class of attractive fluids prefers the strong hexagonal (crystalline) ordering while another exhibits a very low hexagonal coordination (a glass-forming fluid). This crossover occurs if the attraction range assume values of the order of $\delta \approx 0.15$. Notice that the existence of two distinct 3-D colloidal fluids in an attraction range equivalent to $0.3 > \delta > 0.05$ has been predicted by Tejero *et al.*[7] By means of a perturbation theory analysis, these authors have shown that in such an attraction range there are two different types of phase diagrams: the first with only one stable fluid–solid transition (with metastable fluid–fluid and solid–solid coexistence), while the second is characterized by a solid–solid transition with a critical point and a solid–solid–fluid triple point. Based on the results of our study, we can speculate that the first type of the phase diagram in a 2-D fluid is associated with an attraction range $\delta > 0.15$, while the second will occur if $\delta < 0.15$. Partially, this is already confirmed by computer simulations of Bolhuis *et al.*[9] where both the 3-D and 2-D solid–solid transition in a SW model have been detected and both occur if the width of the attractive well is less than 0.07σ that is consistent with the criteria that $\delta < 0.15$.

Analyzing the individual particle trajectories presented in Fig. 3, we note that for $\delta \approx 0.15$ there is a separation tendency for the regions with fluidlike mobility and solidlike immobility, which is a feature of fluid/solid coexistence. On the contrary, in the case of $\delta = 0.05$, the immobile crystalline zones seem to be randomly distributed over all the area. Furthermore, we suggest that the character of the melting transition in a dense 2-D system (conventional first-order transition[3] or two continuous transitions with a ''hexatic'' phase in between, known as KTHNY theory[16]) may depend crucially on the attraction range as well.

A natural question is why the crossover in the behavior of ψ_6 for a dense SW fluid occurs at the attraction range $\delta \approx 0.15$. Making an attempt to understand this, we turn our attention to the key quantity in the calculation of ψ_6, i.e., the definition of the nearest neighbors. In the present study we used the mathematically precise definition of a particle neighborhood in terms of Voronoi polygons. A much simpler definition is the set of disk centers that lie within some maximum distance of the central disk.[4] Recently, Huerta and Naumis[17] have suggested that in a dense HC fluid there is a natural way to define the nearest neighbors of a given disk, as those disks that are in a region around the central one, where the maximal allowed coordination is six, i.e., if their centers fall into a ring between a circle of radius $r = \sigma$ (defined by an hexagon of contacting disks) and a circle of radius $r = 1/(2 \sin \pi/7) \approx 1.152\sigma$ (formed by a heptagon of contacting disks). One can suggest that this is a definition of the attractive SW model (with $\delta = 0.152$) if ''attraction'' is associated with the entropically driven hexagonal self-packing (self-depletion) in a fluid of dense HC disks. In other words, $\delta = 0.152$ for a 2-D hexagonal configuration is exactly the point where the nearest neighbors distance coincides with the range of attraction. Is δ smaller then neighbors are forced to get closer, which destroys ψ_6; if δ is larger, on the other hand, the attractive zone keeps neighboring particle rings together enhancing ψ_6. The results of Figs. 1 and 2 seem to support this suggestion: two model fluids, one attractive SW fluid with $\delta \approx 0.15$ and another purely repulsive HC fluid, in a dense equilibrium-fluid phase both exhibit very similar bond-orientational behavior. Additionally, the attractive SW fluid with $\delta \approx 0.15$ shows a weak dependence against the variation of an attraction strength. If confirmed experimentally, this would be an important observation that, for example, may shed some light on the nature of the ''attractive'' and ''repulsive'' states in (metastable) colloidal matter.[10,11]

Finally, the results presented in this study can be important for the general theory of amorphous solids as well, since the problem presented here is closely related with the formation of random close packing (RCP) arrangements in 2-D systems. Recently, the concept of RCP, which has been used as a paradigm model for amorphous materials, has been put into doubt, because if one increases the packing, the degree of order rises.[5] At the supposed value of the density for the RCP, still there is a certain degree of order. The simulations discussed here can be thought of as an algorithm to produce different degrees of order with the same packing fraction.

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[1] A. Mehta and G. C. Barker, Phys. Rev. Lett. **67**, 394 (1991).
[2] V. Tohver, A. Chan, O. Sakurada, and J. A. Lewis, Langmuir **17**, 8414 (2001).
[3] B. J. Alder and T. E. Wainwright, Phys. Rev. **127**, 359 (1962).
[4] H. Weber, D. Marx, and K. Binder, Phys. Rev. B **51**, 14636 (1995).
[5] S. Torquato, T. M. Truskett, and P. G. Debenedetti, Phys. Rev. Lett. **84**, 2064 (2000); T. M. Truskett, S. Torquato, and P. G. Debenedetti, Phys. Rev. E **62**, 993 (2000).
[6] A. P. Gast, C. K. Hall, and W. B. Russell, J. Colloid Interface Sci. **96**, 251 (1983).
[7] C. F. Tejero, A. Daanoun, H. N. W. Lekkerkerker, and M. Baus, Phys. Rev. Lett. **73**, 752 (1994).
[8] S. M. Ilett, A. Orrock, W. C. K. Poon, and P. N. Pussey, Phys. Rev. E **51**, 1344 (1995).
[9] P. Bolhuis, M. Hagen, and D. Frenkel, Phys. Rev. E **50**, 4880 (1994).
[10] D. Frenkel, Science **296**, 65 (2002).
[11] K. N. Pham, A. M. Puertas, J. Bergenholtz, S. U. Egelhaaf, A. Moussaid, P. N. Pusey, A. B. Schfield, M. E. Cates, M. Fuchs, and W. C. K. Poon, Science **296**, 104 (2002).
[12] A. Trokhymchuk, D. Henderson, A. Nikolov, and D. T. Wasan, Phys. Rev. E **64**, 012401 (2001).
[13] P. D. Kaplan, J. L. Rouke, A. G. Yodh, and D. J. Pine, Phys. Rev. Lett. **72**, 582 (1994).
[14] G. Foffi, K. A. Dawson, S. V. Buldyrev, F. Sciortino, E. Zaccarelli, and P. Tartaglia, Phys. Rev. E **65**, 050802 (2002).
[15] C. Reichhardt and C. J. Olson Reichhardt, Phys. Rev. Lett. **90**, 095504 (2003).
[16] K. Binder, S. Sengupta, and P. Nielaba, J. Phys.: Condens. Matter **14**, 2323 (2002).
[17] A. Huerta and G. G. Naumis, Phys. Rev. Lett. **90**, 145701 (2003).