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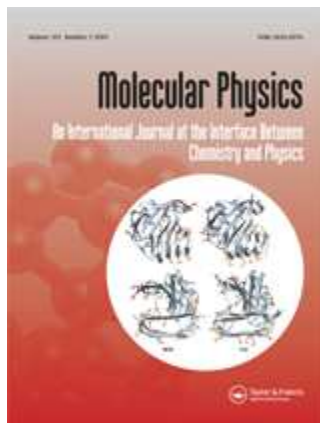
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Fluids of Core-Softened Particles in Dimension Two: an Integral Equation Study

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Fluids of Core-Softened Particles in Dimension Two: an Integral Equation Study

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February 20, 2009

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Abstract

An interaction model with core-softening, that produces clustered phases in dimension two, is studied by integral equation theories, and compared with corresponding simulation results. It is shown that the Hypernetted-chain (HNC) equation is surprisingly accurate and easier to solve numerically than the Percus-Yevick (PY) equation which appears unable to get to the cluster phase region. This is compared to the behaviour of the two theories in the absence of the core-softening: in the high temperature regime the Percus-Yevick theory is more accurate while in the low temperature regime it is the HNC theory that become more accurate. It is the inclusion of an infinite class of cluster

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8 diagrams allows the latter theory to better describe phases where local
9 structures and small clusters play a predominant role in characteriz-
10 ing their macroscopic properties, and the opposite behaviour observed
11 for continuous phases of hard and soft interactions must be due to
12 fortuitous diagram compensations in the real system. The HNC the-
13 ory gives a very accurate structural description of the various cluster
14 phases, as shown by comparing the radial distribution functions and
15 structure factors with those from simulations.
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26 **1 Introduction**

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29 The rich and intriguing cluster patterns than can be formed when simple
30 dipolar hard spheres are constrained into a bi-dimensional monolayer or bi-
31 layer have been extensively studied by Jean-Jacques Weis[1, 2, 3]. The core
32 softening interaction model, that also leads to rich clustering, was initially
33 introduced by Hemmer and Stell[4] to describe a particular type of liquid-
34 liquid type phase ordering, and further studied in that purpose by many
35 authors[5, 6, 7]. The interest for this type of interaction in dimension two
36 was recently revived by Malescio and Pellicane[8]- for the case of hard core
37 interactions, and Camp[9, 10, 11] -for the case of soft core interactions. In
38 both cases, it was shown that such type of *isotropic* interactions could lead
39 rich variety of cluster phases. In two-dimensions, these transformations can
40 be spectacularly visualized by snapshots: as density is increased one sees an
41 ordinary disordered liquid, but then dimerized, striped and networked liq-
42 uids. Moreover, in addition to the usual high density solid, a low density
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solid phase is also observed at very low temperatures[9]. The remarkable
fact is that all these cluster “phases” are disordered: there is no Landau-
type one-body order parameter that can describe them. Instead, the proper
statistical tools to analyze these transformations are the radial distribution
function (RDF) and the corresponding structure factor (SF). The appearance
of specific local structures of length scale ξ leads to the emergence of specific
peaks in the structure factor at wave-vector $k_p < k_m = 2\pi/\sigma$, where k_m is the
position of the main peak corresponding the diameter σ of the particles. In
contrast, at $k = 0$ the structure factor is always very small, indicating that
the compressibility of the liquid is small, and therefore it is not the density
fluctuations that can give rise these cluster phases. This is also compatible
with the fact that the corresponding core-soft interactions are repulsive.

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Integral equation theory studies of core-softened interaction have been
principally confined in dimension 3[13, 12, 14]. The principal motivation for
using core-softening seems aimed at reproducing water-like behaviour[15, 16],
and eventually to relate the low temperature anomalous properties of this
liquid to the possible existence of a second length scale in the interaction.
This is very much along the original idea of Hemmer and Stell, since many
theoreticians predict that water may have high density liquid - low density
liquid phase separation in the low temperature high density part of its phase
diagram[17, 18, 19]. Such studies have been also done in dimension 2[20] and
also in dimension 1[21].

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Recently, we have shown that many of the principal features of the radial
distribution function and the structure factor of room temperature liquid wa-
ter, could be reproduced in a striking fashion by two soft repulsive cores[22].

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Moreover, we have shown that the HNC theory was able to describe this behaviour in remarkable agreement with the simulation, while the PY could not be solved for the state points of interest[22]. Despite the importance of water, the recent works[8, 9, 10] indicate that core softening has interest beyond this single application, since it can describe the appearance of local heterogeneity within stable phases.

In the present work, we would like to examine the fate of the two diagrammatically proper integral equation closure relations, the Percus-Yevick and the Hypernetted-chain equations, when describing two-dimensional liquids with core-softened interaction. For this, we choose the same model studied by Camp, and investigate how these equations are able to deal with the appearance of clustering. The principal motivation is the following: integral equations are well known to be less reliable in the vicinity of phase transitions, where the correlations at long range put their diagrammatic insufficiency at test. Despite many investigations since almost half a century, almost nothing is known about the importance of these diagrams and the role they play. Therefore, it is of high interest to know how these approximate theories behave in the vicinity of cluster “phases”.

2 Theoretical details

The interaction used by Camp is modeled to mimic that of dipolar spheres laying on a plane[9]. This interaction consist in a Lennard-Jones part together with a repulsive $1/r^3$ part which comes from the effective dipolar part

$$v(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] + \epsilon' \left(\frac{\sigma}{r} \right)^3 \quad (1)$$

The parameter ϵ' is chosen such that the resulting interaction presents an inflexion point at $r = 6^{1/6}\sigma$ [9], leading to $\epsilon' = 8\sqrt{6}/9\epsilon$.

The integral equation theory for simple liquids consists in determining the RDF $g(r)$ and the direct correlation function (DCF) $c(r)$. This is achieved by solving two equations, the exact Ornstein-Zernike equation (OZ), written here in the Fourier space in terms of the structure factor $S(k) = 1 + \rho \int d\vec{r} \exp(i\vec{k}\cdot\vec{r})(g(r) - 1)$ as[23]

$$S(k) = \frac{2}{1 - \rho\hat{c}(k)}$$

together with an approximate closure relation, here the HNC or the PY closures[23]

$$g(r) = \exp\left(-\frac{v(r)}{k_B T}\right) \exp(g(r) - 1 - c(r)) \quad (\text{HNC})$$

$$g(r) = \exp\left(-\frac{v(r)}{k_B T}\right)(g(r) - c(r)) \quad (\text{PY})$$

Written as such, the last relation indicates that PY is a linearized version of the HNC closure. However, if the log of the two relations is taken, it amounts to express $c(r)$ in terms of the RDF, and it is then HNC that would appear as the linearisation of the PY equation. Diagrammatically, however, it is the HNC approximation that contains more cluster diagrams (in terms of the Mayer function $f(r) = \exp(-v(r)/k_B T) - 1$), and therefore is expected

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to be more accurate. For the hard sphere fluid, the analytical solution of the PY is more accurate than the HNC equation[23]. This has led to think that the PY equation is more accurate than the HNC equation for purely repulsive interactions. The present study indicates that the presence of the infinite set of additional diagrams in the HNC equation allows to predict the local micro-structure more accurately than the PY equation. Therefore the occasional accuracy of the PY must be due to a compensation of higher order diagrams in the full theory.

3 Results

The integral equations have been solved on a grid of $N = 1024$ points with r -step of $r = 0.02\sigma$. The reduced density is defined as usual as $\rho^* = (N/V)\sigma^3$ and the reduced temperature as $T^* = k_B T/\epsilon$. The relative weight of the core softening energy is then controlled by the parameter $\epsilon_C = \epsilon'/\epsilon \approx 2.1773$. These conventions are the same as in Ref.[9], which allows a direct comparison with the reported results. The details of the methodology to solve integral equations in dimension two, and particularly the Fourier-Bessel transformation techniques needed to solve the OZ equation have been reported in several earlier works[25, 26, 27, 28], and will not be repeated here. In addition, we have performed constant NVT ensemble Monte Carlo (MC) simulations, with a number of particles of $N = 1089$, in order to produce the radial distribution function (RDF) $g(r)$ needed for comparison with those from theory. The corresponding structure factor was obtained by direct Fourier transform of $g(r)$. Since the two-dimensional Fourier transform require log scale grid[25],

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it was necessary to interpolate the RDF obtained by simulation on a regularly spaced grid. This was done using a linear interpolation as a first approximation. The obtained results show that this crude interpolation is sufficient for a quantitative analysis. The very small k behaviour was however very noisy in many cases, which is due to numerical noise in the medium to long range part of the RDF obtained from the simulations, rather than the interpolation procedure itself.

3.1 The Hard and Soft Core fluids

In order to better assert what happens in the cases when the full core-softening interaction is turned on, we examine the cases for $\epsilon_C = 0$.

First, we examine the RDF from the reference hard disc fluid, for a relatively high density $\rho^* = 0.85$, which is close to the maximum density at which the HNC closure can be solved[29]. Fig.1 shows unambiguously that the PY equation is very accurate, while the HNC equation appears to overestimate the ordering of the molecules, hence producing peaks that are shifted inward towards smaller distances -meaning tighter packing, and that are also higher than those of the MC results, indicating higher correlations. This is the reason why the HNC equation loses solutions much earlier than the PY theory, which can be solved up to higher densities. This seems equally true for hard non-spherical particles as well, where the HNC theory tends to overestimate the orientational ordering, as was verified in two[28] and three[30] dimensions.

Next, we examine the case of soft-core interactions, for three different

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temperatures, $T^* = 5, 1, 0.1$, and close to the highest density that was obtainable in each case. This is shown in Fig.2(a,b,c). At high temperature (top panel), the two integral equations are comparable in accuracy, as is expected, since the interaction is depressed. At the intermediate temperature (middle panel), it is seen that the PY equation is again very accurate. This time, and very surprizingly, the HNC results appear to underestimate the correlations, as can be seen from the rapid decay of the correlations. This result indicates that the diagrams missing in the HNC theory play an important role in describing the long range behaviour of the theory. Suprizingly, the lack of diagrams in the PY theory seems to compensate each other at large distances. Finally, at the smallest temperature, it is HNC that becomes more accurate, particularly at large distances, where the PY theory shows more pronounced packing effects.

A look at the corresponding structure factors in Fig.3(a,b,c) gives interesting insights into the nature of each closure. The structure factor reveals essentially the long range behaviour of the RDF, so it gives a better insight at the large scale correlations and packing effects. For $T^* = 5$ we learn nothing more than for the RDF in Fig.2a. For $T^* = 1$ we see that the simulations give a second split peak that is reproduced by neither of the theories. Interestingly though, PY gives an averaged peak, while HNC fits nicely only the second part of the split peak. As to the first peak, both MC and PY reach about 8 while HNC reached only half that value. From the third peak on, the agreement between PY and MC is perfect. The second split peak indicates the existence local crystalline order within the second neighbour shell. At the smallest temperature (lower panel) we see that the differences between

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9 the two theories is less obvious, and it is the PY theory that would seem to
10 better fit the overall features of MC data, except for the second peak again.
11 So, the good agreement observed in the RDF between HNC and MC for this
12 case seem to stem essentially from the second peak feature of the $S(k)$.
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16 A look at the snapshots for the temperature $T^* = 1$ indicates that the
17 system looks glassy like, with predominance for local semi-crystalline hetero-
18 geneity, which explain the feature in the second peak of $S(k)$, of which HNC
19 seems to capture only some of the features. For the lowest temperature, it
20 is also HNC that has solution for higher densities (up to $\rho^* = 0.6$, while PY
21 stop having solutions at $\rho^* = 0.51$.
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29 The main conclusion of this part is that, while PY may seem a better
30 theory for purely repulsive cores, the secondary structure is better captured
31 by a richer diagrammatic theory. There are intriguing compensation effects
32 in the PY theory that one is eager to know the origin of.
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39 3.2 The core-softened fluid

40 41 42 3.2.1 The phase diagram

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44 The phase diagram obtained by the two theories is shown in Fig.4, and com-
45 pared to that taken from the simulations of Ref.[9]. As usual, it is the limit
46 of solution of the two theories that are obtained, and not the actual “phase”
47 boundaries. The first remark is that either theories give a *single* boundary,
48 where the simulations of Ref[9] indicate the existence of four phases: two
49 solid phases, one at high density (S) and one a low density and low temper-
50 ature (LS), one cluster phase (C) and the usual fluid phase (F). The second
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remark is that either integral equations have only a “fluid” phase that terminates at a boundary with is very different for each of them. In particular, we note that HNC has a boundary very close to the S phase, while that of PY is well within the F phase. Both theories have no solutions to the right of their respective boundaries. The first conclusion is that the PY theory cease to have solutions at very small densities, while the HNC theory has solutions well inside the C phase region. This situation is already very different from that found in the hard and soft core cases where both theories could be solve quite close to the fluid-solid boundary, except precisely at very low temperatures, where the PY theory starts to have difficulties to handle high densities. So, we expect that the explicit clustering observed here is the reason why PY cannot solved even deep inside the F phase where no clustering is observed. This fact alone indicates that PY theory is diagrammatically insufficient.

Fig.5 shows how the core-softened interactions vary as the temperature is lowered. Thus, at very low temperatures, the particles see mostly the outer repulsion, except at very high packing where they need to surmount this barrier in order to reach close packing. This explains why a low diagrammatic theory might be able to describe properly such configurations that require cooperative coordination of a large ensemble of particles.

The very low temperature region below $T^* = 0.003$ could not be reached by both theories for numerical reasons. Indeed, the interaction at the core part becomes very repulsive, and they tend to dominate the effective part of the interactions that come from the correlations between molecules, and which give rise to the clustering. It is probably possible to explore this region by using some reference trick to eliminate the numerical barrier due the huge

repulsion, but we have not tried this at this stage.

3.2.2 Structural properties

First, we report in Fig.6 a comparison of the structure between the simulations and the two theories at two state points in the fluid phase, one at high temperature $T^* = 1$ and $\rho^* = 0.8$ and the other at a lower temperature $T^* = 0.05$ and $\rho^* = 0.1$. For $T^* = 1$ there is no cluster phase yet, even at density as high as $\rho^* = 0.8$, and the theories behave similarly to the previous case, with PY being clearly more accurate. At high temperature, the softening barrier is very low, so all particles can pack up to the smallest core. At lower temperature, and at fluid phase density, the softening barrier is relatively high, and all particles pack up to this distance. Both these features are well reproduced by both theories. However, at $T^* = 0.05$, the small peak at $r \approx \sigma$ is more apparent for HNC, indicating that this theory sees that some particles can still come close to main core. The PY theory fails when the density is high enough so that some particles need to get close to $r = \sigma$. Moreover, the oscillations of the RDF are wider, indicating that this theory mostly sees the outer energy barrier. This could explain why it ceases to have solutions at lower densities: it is because these correspond to an effective larger packing fraction corresponding to a larger particle size. This example proves directly the diagrammatic insufficiency of PY. On the contrary, HNC is very accurate.

Fig.7 shows a sequence of RDF as ρ^* is varied at fixed temperature $T^* = 0.01$. Fig.8 shows the corresponding structure factors. Fig.9 shows the snapshots corresponding to the four densities. The first $\rho^* = 0.05$ is in the very

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8 low density fluid phase, for which PY can still be solved. The second $\rho^* = 0.2$
9 is well inside the fluid phase, in the region where dimers and some trimers
10 are observed. The third $\rho^* = 0.3$ is in the curled stripes cluster phase. The
11 last $\rho^* = 0.45$ is in the networked cluster phase. The first case is the only
12 one that contains a PY solution. Much like in Fig.6, one can see that PY
13 exaggerates the packing due to the outer core, showing again its diagrammatic
14 insufficiency. This is seen both by the wider oscillations in the RDF and the
15 high and narrow first peak at $k\sigma \approx 2\pi/5$ in the SF. Deeper in the F phase,
16 where dimers appear, HNC is able to both track this formation by showing
17 a first peak in the RDF at $r = \sigma$ and in good agreement with MC. The
18 large second peak indicates that most particles are still repelled by the outer
19 core. The agreement with MC is out of phase after these two first peaks,
20 indicating that HNC has some important diagrammatic insufficiency which
21 may be able to both describe entropical aggregation and loose particles. In
22 the cluster phase, however, the agreement becomes excellent, both in r and k
23 spaces. First, the structural signature of the stripe phase at $\rho^* = 0.3$ is well
24 captured. This is particularly seen in the SF representation, where the main
25 peak at $k\sigma \approx 2\pi$ due to the contact at $r = \sigma$ is of equal height than the
26 pre-peak at $k\sigma \approx 2\pi/2$ that is due to soft repulsion at $r \approx 2\sigma$. This equality of
27 peaks and pre-peak height illustrates very well the perfect *symmetry breaking*
28 that occurs in the effective interactions in the stripe phase. Indeed, each
29 particle is *exactly* in the two configurations imposed by the two length scales
30 that appear in the interaction energy, one at $r = \sigma$ and the other at $r \approx 2\sigma$.
31 The fact that an *isotropic* interaction leads to an *effective anisotropic* one
32 is very remarkable. Finally, the structure of the networked fluid is equally
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8 well captured at $\rho^* = 0.45$, but the corresponding features are harder to read
9 from the RDF and the SF.
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12 It is puzzling that HNC performs so well for well morphed cluster phases,
13 but not so for the dimer-trimer region which at a lower density. This is
14 certainly an indication about its diagrammatic structure and would deserve
15 further investigations.
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21 Finally, we note that the HNC equation is numerically solved very easily,
22 even very near the no-solution regions, as the iteration cycles converge very
23 rapidly. In contrast the PY theory appears very difficult to converge and
24 larger number of iterations are often required. This is in contrast also to
25 what happens when the second soft repulsion is absent, where both theories
26 are sluggish near the fluid-solid phase boundary. The feature noted above is
27 important if put in relation with the cluster nature of these theories.
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36 **3.2.3 Phases and boundaries**

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39 Integral equations are notoriously known for their deficiencies near phase
40 boundaries[31]. These deficiencies are usually related to the appearance of
41 long range correlations due to enhanced density fluctuations and the subse-
42 quent growth of the correlation length. However, such behaviour is usually
43 related to presence of attractive part of the interaction. In the present case,
44 and in the absence of attractive interactions, the $k \rightarrow 0$ behaviour of the
45 structure factor is never anomalous, both in the simulations and the inte-
46 gral equation results, which is to say that the compressibility of these liquids
47 is always small. Rather, it is the presence of the pre-peak that witness the
48 appearance of clusters instead of large scale density fluctuations that could
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9 contribute at $k = 0$. The fact that HNC is able to predict the appearance
10 of the clusters phases, when it is not capable of describing properly long
11 range correlations, is both noteworthy and intriguing. Indeed, it is often
12 thought that integral equations can be solved only until the stability limit
13 of the phase they are solved for. The results shown here would then tend
14 to suggest that the various cluster phases observed here are not true ther-
15 modynamical phases. This conclusion, drawn from an approximate integral
16 equation result, is in variance with the second order stripe phase transi-
17 tion reported in Ref.[8], albeit for a different model. Similar consideration
18 holds equally for the low density solide phase reported in Ref.[9] which is
19 not found here for the same temperature and density range. Such conclu-
20 sion might be, at first, enforced by the fact that integral equation theories
21 are solved in the true thermodynamical limit, while computer simulations
22 suffer from inevitable finite size effects that might affect the true periodicity
23 of a phase. However, one should be cautious, because the thermodynamical
24 inconsistency of the HNC theory might hinder its ability to describe proper
25 phase transition as such. In particular, the boundaries of the phase related
26 to the HNC approximations might be shifted towards lower temperatures,
27 which are not currently reachable. Nevertheless, the present findings are
28 intriguing in the sense that the structural and thermodynamical agreement
29 between the theory and the simulations leave open the question about the
30 thermodynamical nature of cluster phases.
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4 Conclusion

The previously analyzed core-softened interaction of Ref[9] is re-explored within the well known diagrammatically proper integral equation theories such as the PY and the HNC closures. The analysis reveals that the cluster based diagrammatic origin of these approximations shows their respective efficiency. These are masked when describing continuous phases. Hence it is often difficult to conclude that a lower diagrammatic theory is better if it compares well with simulation results. This is very much similar to the situation with mean field theories that can often better describe physical situations than those that incorporate higher order fluctuations. This is the reason why integral equation theories are so difficult to solve near phase boundaries where fluctuations are important. The same reason also indicates that a good structural agreement is not necessarily a sign that a better description is obtained. This comment particularly concerns the various diagrammatically improper closures, that have become so popular since they allow a better fit of the properties and structure of various systems, and that are more often used in place of diagrammatically proper closures[13]. The fact that the HNC equation is so adapted to describe cluster “phases” clearly indicates its diagrammatic superiority. In the present analysis, the absence of the so-called bridge cluster diagrams do not seem to play an important role as they do in continuous phases. The absence of attractive interaction induced fluctuations is also important here, and may also influence the fate of these methods. Further investigations into the success and failure of these model interactions is certainly needed to achieve a better understanding and

improving integral equation theories.

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Figure captions

- Fig.1 (color online) The RDF for the 2D hard disc fluid at $\rho^* = 0.85$. Simulation data in green, HNC in blue and PY in magenta. The inset is a closeup at the first peak.
- Fig.2 (color online) The RDF of the 2D soft sphere fluid at $(T^* = 5, \rho^* = 0.8)$ (top panel), $(T^* = 1, \rho^* = 0.8)$ (middle panel), $(T^* = 0.1, \rho^* = 0.5)$ (lower panel). The color conventions are the same as in Fig.1
- Fig.3 (color online) The structure factors corresponding to the RDF in Fig.2
- Fig.4 (color online) The phase diagram of the 2D core-softened fluid. That from the simulations is reproduced from Ref.[9]. The blue symbols represent the solution boundary obtained for the HNC theory, and the magenta symbols for PY. The lines through the symbols are indicative.
- Fig.5 The 2D core-softened interaction energy for three different temperatures $T^* = 0.1, 0.05, 0.01$ labeled on the corresponding curves.
- Fig.6 (color online) The RDF for the core-softened fluid for state points $(T^* = 1, \rho^* = 0.8)$ (top panel) and $(T^* = 0.05, \rho^* = 0.1)$ (bottom panel). The color conventions are as in Fig.1
- Fig.7 (color online) The RDF for the core-softened fluid for $T^* = 0.01$ at four different densities labeled on corresponding panels. The

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8 color conventions are as in Fig.1
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11 Fig.8 (color online) The structure factors corresponding to the RDF
12 shown in Fig.7, with the same color conventions.
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16 Fig.9 (color online) The snapshots for the state points corresponding
17 to the RDF shown in Fig.7.
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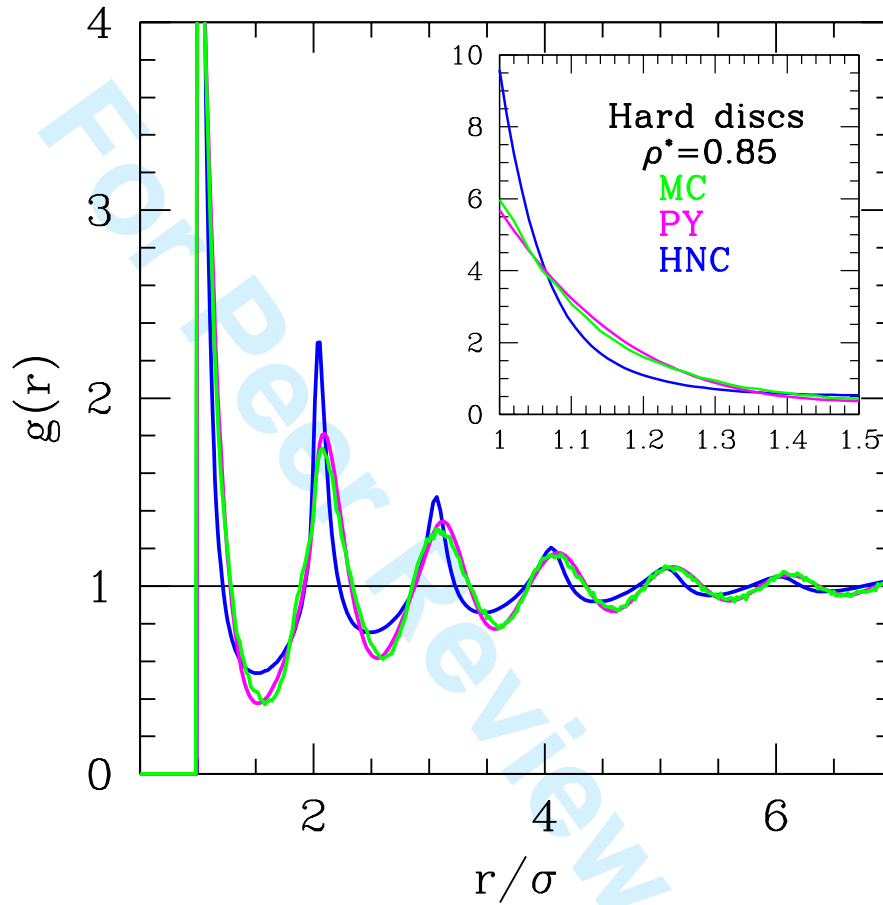


Fig.1 Perera

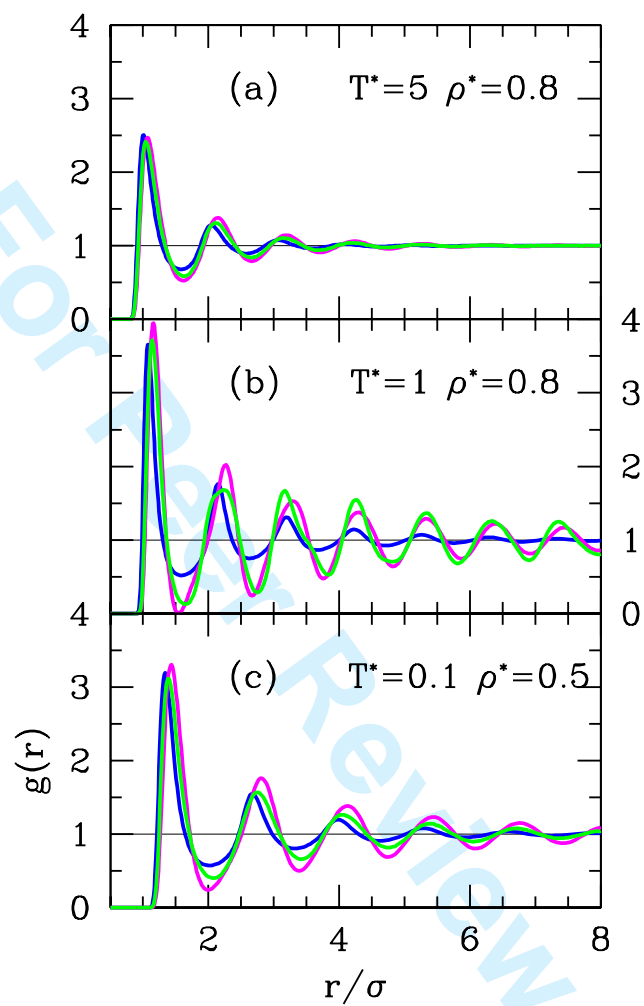


Fig.2 Perera

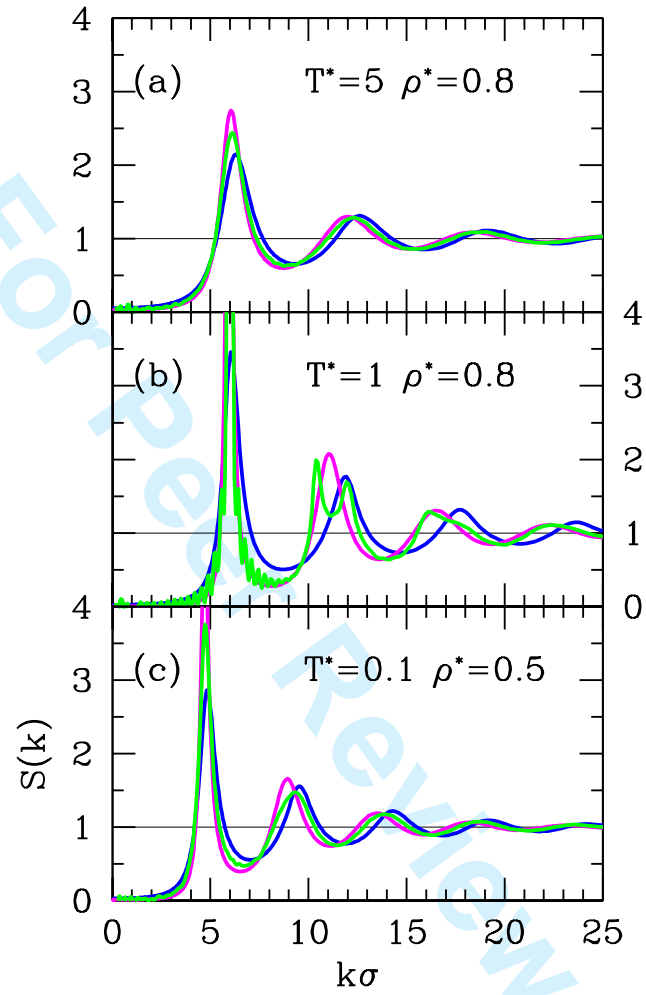


Fig.3 Perera

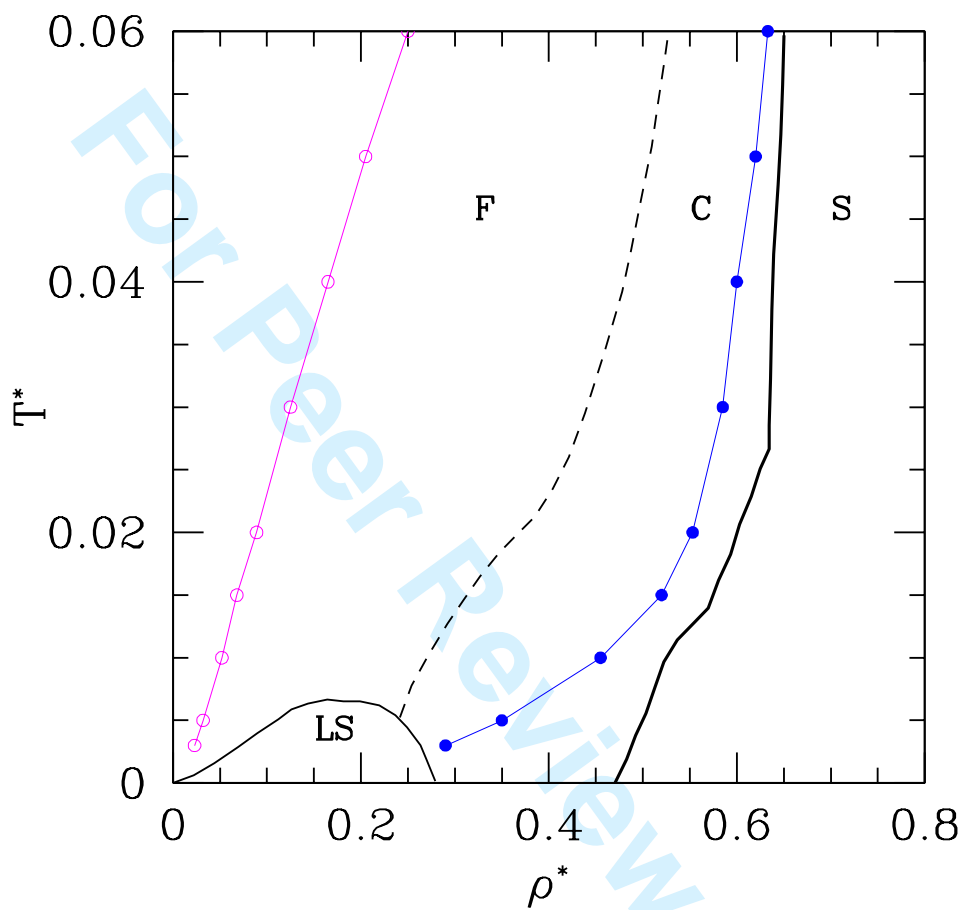


Fig.4 Perera

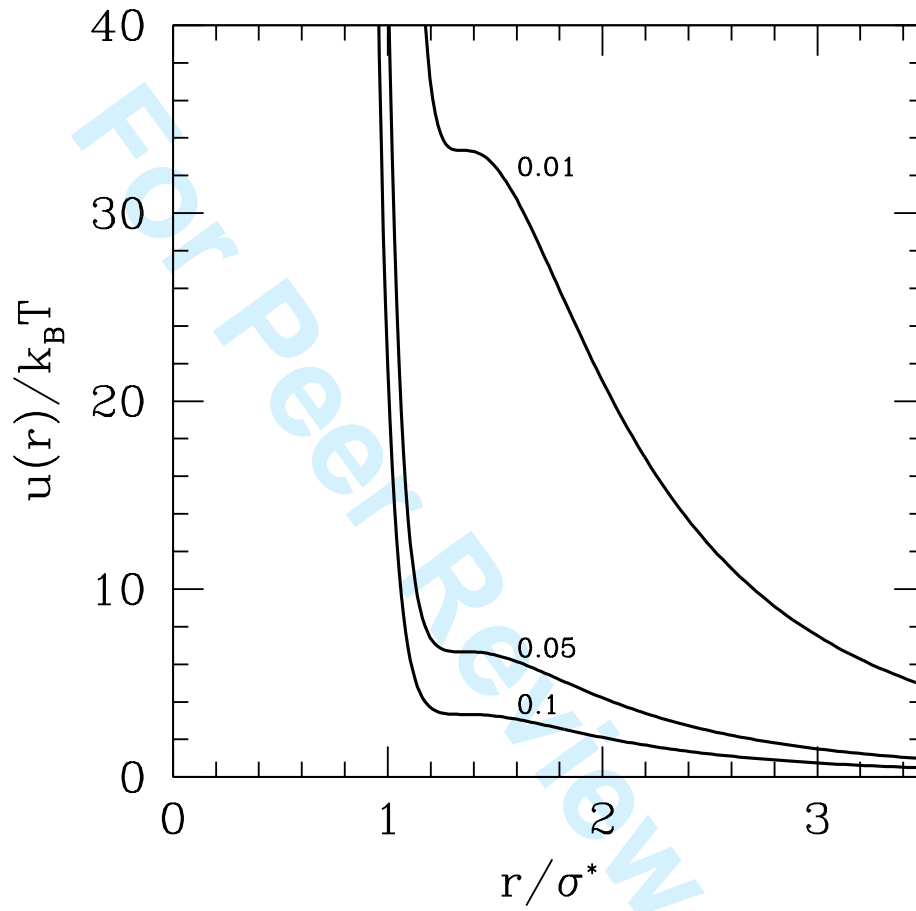


Fig.5 Perera

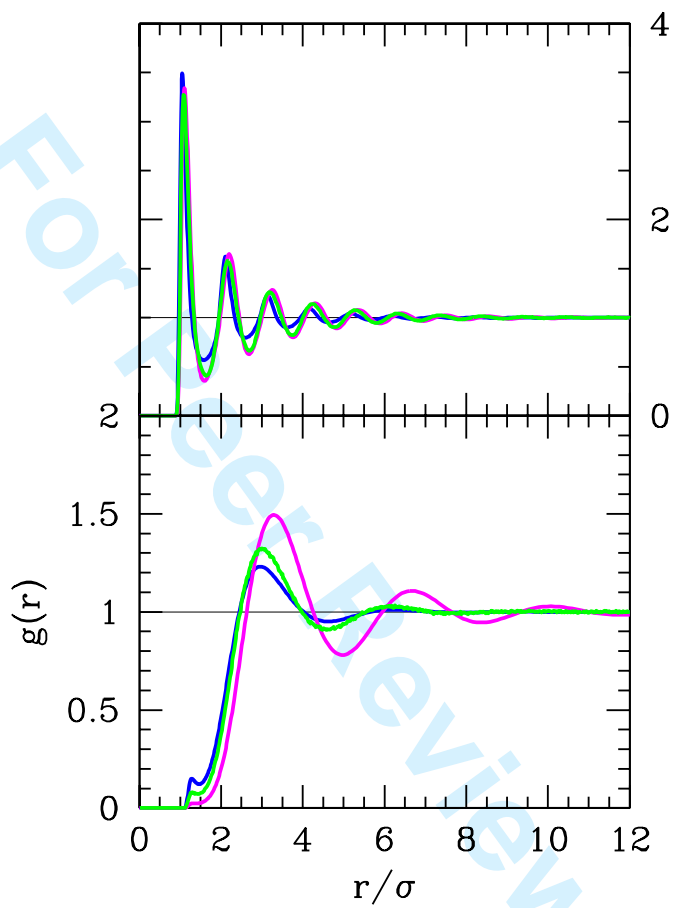


Fig.6 Perera

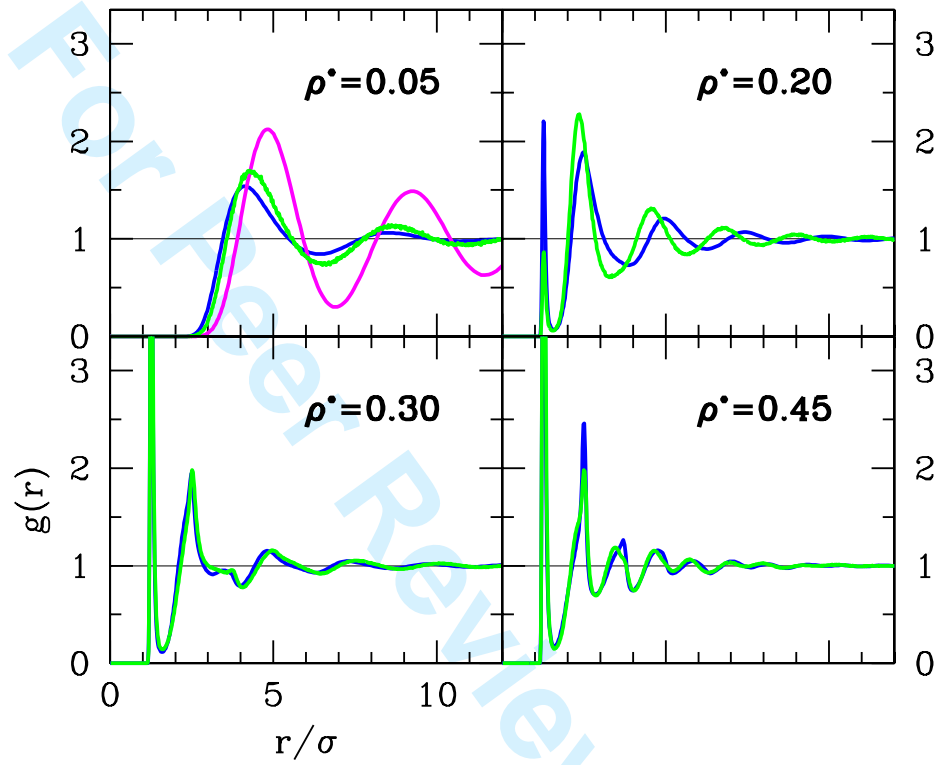


Fig.7 Perera

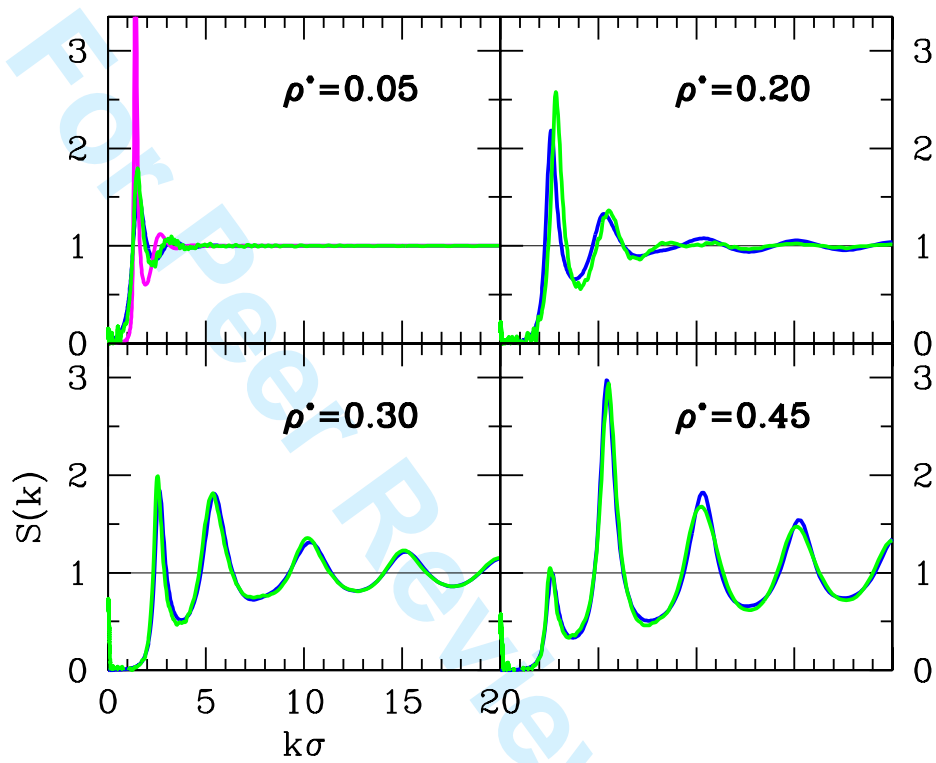
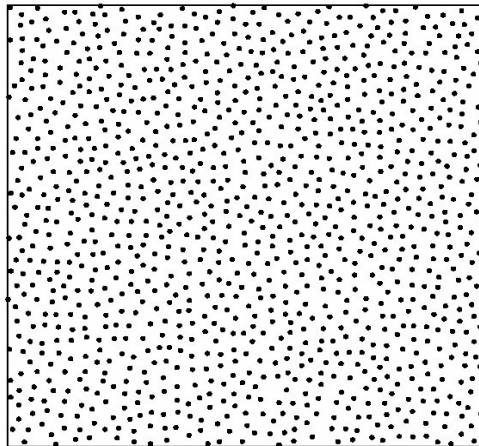


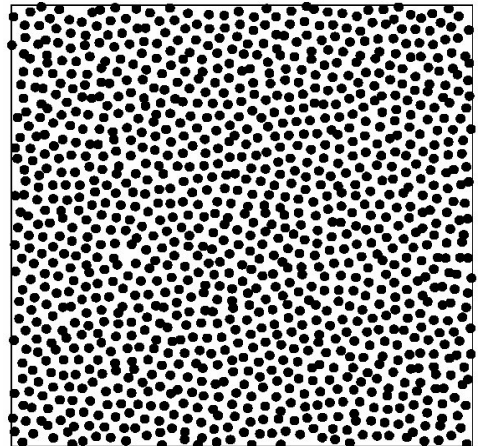
Fig.8 Perera

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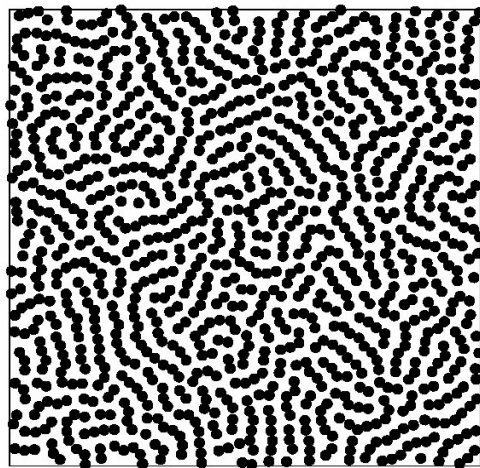
$\rho^* = 0.05$



$\rho^* = 0.2$



$\rho^* = 0.3$



$\rho^* = 0.45$

