Structure and phase behavior of colloidal dumbbells with tunable attractive interactions

G. Munaò¹*, D. Costa², A. Giacometti³, C. Caccamo² and F. Sciortino¹

¹Dipartimento di Fisica, Università di Roma “La Sapienza”
Piazzale Aldo Moro 2, 00185 Roma, Italy
²Dipartimento di Fisica Università degli Studi di Messina
Viale F. Stagno d’Alcontres 31, 98166 Messina, Italy
³Dipartimento di Chimica Fisica,
Università Ca’ Foscari Venezia
Calle Larga S.Marta DD2137, Venezia I-30123, Italy

We investigate thermodynamic and structural properties of colloidal dumbbells in the framework provided by the Reference Interaction Site Model (RISM) theory of molecular fluids and Monte Carlo simulations. We consider two different models: in the first one we set identical square-well attractions on the two tangent spheres composing the molecule (SW-SW model); in the second scheme, one of square-well interactions is switched off (HS-SW model). Appreciable differences emerge between the physical properties of the two models. Specifically, the \( k \to 0 \) behavior of SW-SW structure factors \( S(k) \) points to the presence of a gas-liquid coexistence, as confirmed by subsequent fluid phase equilibria calculations. Conversely, the HS-SW \( S(k) \) develops a low-\( k \) peak, signaling the presence of aggregates; such a process destabilizes the gas-liquid phase separation, promoting at low temperatures the formation of a cluster phase, whose structure depends on the system density. We further investigate such differences by studying the phase behavior of a series of intermediate models, obtained from the original SW-SW by progressively reducing the depth of one square-well interaction. RISM structural predictions positively reproduce the simulation data, including the rise of \( S(k \to 0) \) in the SW-SW model and the low-\( k \) peak in the HS-SW structure factor. As for the phase behavior, RISM agrees with Monte Carlo simulations in predicting a gas-liquid coexistence for the SW-SW model (though the critical parameters appears overestimated by the theory) and its progressive disappearance moving toward the HS-SW model.

INTRODUCTION

Physical properties of colloidal molecules constitute one of the most interesting and investigated branch of soft matter physics. The recent development in experimental techniques offers nowadays the possibility to engineer colloidal particles with different sizes, shapes and chemical compositions [14] and this opportunity to finely tune the interaction properties of colloidal systems gives rise to rich phase behaviors [7]. Within this large class of molecules, colloidal particles constituted by two interaction sites (dumbbells) have been recently investigated by means of both experimental techniques [8, 17] and theoretical and numerical studies [13, 30]. In particular, it has been shown that dumbbells colloids can be used as building blocks to fabricate new photonic crystals [14] and other complex structures [10]; furthermore, recent progress in experimental synthesis permits the fabrication of asymmetric functionalized dimer particles on a large scale (see [16, 17] and references). As for simulations and theoretical investigations of colloidal dumbbells, previous studies about the so-called vibrating square-well dumbbells [25, 29] have shown a phase behavior strictly dependent on both the aspect ratio and the strength of the square-well interaction, with dramatic consequences on the phase diagram. Other recent studies have concerned the phase behavior of dipolar colloidal gels [24, 28], the dynamical arrest in a liquid of symmetric dumbbells [22], the dynamics of a glass-forming liquid of dumbbells [21], the density profiles of confined hard-dumbbell fluids [27] and the two-dimensional structure of dipolar heterogeneous dumbbells [30]. More generally, such particles constitute an useful prototype model for a variety of molecular systems, whose structural and thermodynamic properties are still under scrutiny.

In this article we investigate the physical properties of model colloidal dumbbells by means of integral equation theories of molecular fluids and Monte Carlo simulations. Specifically, we first consider dumbbells constituted by two identical tangent Hard Spheres (HS) interacting with the sites of another dumbbell by means of a Square-Well (SW) attractive potential (SW-SW model hereafter); such a model, with different SW parameters, has been analyzed also in the past by means of different theoretical techniques [13, 19]. We then examine a second model, in which one of the square-well interactions is switched off, so to leave a bare hard-sphere repulsion on the corresponding site (HS-SW model). The HS-SW model may be seen as an extension to a dumbbell scheme of Janus colloids [31, 41], in which half of the molecular surface is attractive and the other half is repulsive. The molecular geometry and interactions involved in the HS-

*Email: gmunao@gmail.com
model allow only for a limited number of bonds to be developed. Such “limited-valence” class of models has received a significant attention in the last years; in particular, it has been demonstrated that upon decreasing the valence below six the liquid-vapor unstable region progressively shrinks to lower densities, thereby creating an intermediate region where a stable network may be formed [42–43], giving rise to equilibrium gels [44]. In order to further elucidate the differences in the phase behavior between the SW-SW and HS-SW models, we also study a series of intermediate models, obtained by progressively reducing to zero one of the square-well interactions of the original SW-SW model. For the sake of completeness, and for comparison with previous models, we also shortly revisit the structural properties of the tangent hard spheres model (HS-HS model), previously investigated by some of us and other authors (see [45–48] and references).

Integral equations theories of the liquid state [49] play a significant role in the study of simple and complex fluids, being relatively simple to implement and generally able to provide a good description of fluid-phase equilibria [50]. In our study we adopt the Reference Interaction Site Model (RISM) theory of molecular fluids, developed by Chandler and Andersen [51] as a generalization of the Ornstein-Zernike theory of simple fluids [49]. In the original formulation, molecules were viewed as composed by a suitable superposition of several hard spheres, rigidly bonded together so to reproduce a given molecular geometry [52]. Later on, the theory has been extended to deal with more realistic representation of complex liquids, including associating fluids such as water [53–54], or methanol [55–57]. Recently, we have developed a thermodynamically self-consistent RISM approach, able to positively predict the structural properties of homonuclear hard dumbbells [45–46]. RISM has been widely used to study colloidal models as, for instance, the thermodynamic and structural properties of discotic lamellar colloids [58–59], the self-assembly in diblock copolymers (modeled as “ultrasoft” colloids) [60], the interaction between colloidal particles and macromolecules [61], the crystallization and solvation properties of nanoparticles in aqueous solutions [62], the liquid structure of tetrahedral colloidal particles [63] and the self-assembly properties of Janus rods [64].

In this work, we have constantly assessed our theoretical predictions for the structural properties of various models against standard Monte Carlo simulations. RISM results concerning the fluid phase equilibria have been compared with Successive Umbrella Sampling (SUS) [65] simulations, coupled with histogram reweighting techniques [66].

The paper is organized as follows: in Sect. II we detail the model, the RISM theory and the plan of simulations. Results are presented and discussed in Sect. III. Conclusions follow in Sect. IV.
As far as the RISM theoretical framework is concerned, the pair structure of a fluid composed by identical molecules, each formed by $n$ interaction sites is characterized by a set of $n(n+1)/2$ site-site intermolecular pair correlation functions $h_{ij}(r) = g_{ij}(r) - 1$, where $g_{ij}(r)$ are the site-site radial distribution functions. The $h_{ij}(r)$ are related to a set of intermolecular direct correlation functions $c_{ij}(r)$ by a matrix equation that in $k$-space reads:

$$
H(k) = W(k)C(k)W(k) + \rho W(k)C(k)H(k). \quad (5)
$$

For the two-site models investigated in this work ($i, j = 1, 2$) and therefore in Eq. (5) $H \equiv [h_{ij}(k)], \ C \equiv [c_{ij}(k)], \ W \equiv [w_{ij}(k)]$ are $2 \times 2$ symmetric matrices; the elements $w_{ij}(k)$ are the Fourier transforms of the intramolecular correlation functions, written explicitly as:

$$
w_{ij}(k) = \frac{\sin[kL_{ij}]}{kL_{ij}}, \quad (6)
$$

where in our case the bond length $L_{ij}$ is given either by $L_{ij} = \sigma$ if $i \neq j$ or by $L_{ij} = 1$ otherwise. The RISM equation has been complemented by the HNC closure [49] for the direct correlation functions $c_{ij}(r)$:

$$
c_{ij}(r) = \exp[- \beta V_{ij}(r) + \gamma_{ij}(r)] - \gamma_{ij}(r) - 1 \quad (7)
$$

where $\beta = 1/T$, $V_{ij}(r)$ are the site-site potentials of Eqs. (1)-(4) and $\gamma_{ij}(r) = h_{ij}(r) - c_{ij}(r)$. We have implemented the numerical solution of the RISM/HNC scheme by means of a standard iterative Picard algorithm, on a mesh of 8192 points with a spacing $\Delta r = 0.005\sigma$.

As for the determination of fluid phase equilibria in the RISM framework, we have calculated the excess freeenergy via thermodynamic integrations along constant-density paths according to [49]:

$$
\frac{\beta A^{ex}(\beta)}{N} = \frac{\beta A^{ex}(\beta = 0)}{N} + \int_0^\beta \frac{U(\beta')}{N} d\beta', \quad (8)
$$

where $N$ is the number of molecules and the internal energy of the system is given by:

$$
U/N = 2\pi \rho \sum_{i,j=1}^2 \int_0^\infty V_{ij}(r) g_{ij}(r) r^2 dr. \quad (9)
$$

In Eq. (8) $A^{ex}(\beta = 0)$ corresponds to the excess free energy of the HS-HS model, for which we have used the analytic expression fitting the Monte Carlo data derived by Tildesley and Street [47]. Once the free energy is known, the pressure can be deduced by derivation according to:

$$
\frac{\beta P}{\rho} = \rho \frac{\partial(\beta A/N)}{\partial \rho} \bigg|_T. \quad (10)
$$

In order to apply Eq. (10), we have first performed a polynomial best-fit of free energy as a function of the density for each temperature; then, we have calculated the derivative of such analytical functions to get the pressure and the chemical potential thereby, according to the standard thermodynamic relation:

$$
\beta \mu = \frac{\beta A}{N} + \frac{\beta P}{\rho}. \quad (11)
$$

Finally, the requirement of equal $P$ and $\mu$ at fixed $T$ in both phases determine the coexisting densities at a given temperature.

Actually, the RISM/HNC formulation provides another straightforward, closed expression for the free energy, not requiring any thermodynamic integration, as detailed in Refs. [67, 68]. However, the preliminary application of such a closed formula for the SW-SW and HS-SW models (not reported in the paper) has shown that the free energy estimates thereby obtained are less accurate in comparison with those calculated according to the more cumbersome scheme of Eqs. (8)-(11). The fact that the various routes from structure to thermodynamics yield different predictions is not surprising, given the thermodynamic inconsistency of most integral equation theories, including the RISM/HNC scheme. In this context, it is generally recognized that the energy route provides the most accurate predictions (see [50] and references therein). Then, the integration/derivation calculations involved in Eqs. (8) and (10) can be accurately carried out by analyzing the temperature range over sufficiently narrow steps.

As far as simulations are concerned, we have calculated structural and thermodynamic properties of our models by means of standard Monte Carlo (MC) simulations at constant volume and temperature (NVT ensemble), on a system constituted by $N = 2048$ particles enclosed in a cubic box with standard periodic boundary conditions. As for the coexistence curves, they have been evaluated via successive umbrella sampling (SUS) simulations in the grand canonical ($\mu$VT) ensemble. According to this method, the range $[0, N_{max}]$ of particles is divided into many small windows of size $\Delta N$. For each window $i$ in the interval $N \in [N_i, N_i + \Delta N]$, a grand-canonical MC simulation is carried out, avoiding the insertion or deletion of particles outside the range of the window [69]. This allows the calculation of the histogram $H_i$ monitoring how often a state with $N_i$ particles is visited in the window $i$. The full probability density is then calculated as the following product:

$$
\frac{P(N)}{P(0)} = \frac{H_0(1)}{H_0(0)} \cdot \frac{H_0(2)}{H_0(1)} \cdot \cdots \frac{H_i(\Delta N)}{H_i(N - 1)} \quad (12)
$$

The advantage of using such a method relies both in the possibility to sample all microstates without any biasing function and in the relative simplicity to parallelize the
run, with a speed gain scaling linearly with the number of processors. Once \( P(N) \) is obtained, at fixed temperature and chemical potential, histogram reweighting techniques \[66\] can be applied to eventually obtain the coexistence points. This is done by reweighting the densities histogram until the regions below the two peaks (in the low- and high-density phases) attains the same area.

### RESULTS AND DISCUSSION

#### Structure factors

We first recall that, as shown in our previous papers \[45, 46\], the RISM approach gives generally good results for the HS-HS fluid. Here we show in Fig. 2 a comparison between RISM and MC site-site structure factors \( S_{ij}(k) \) for two different densities, \( \rho^* = 0.2 \) and \( \rho^* = 0.4 \) (corresponding to the packing fractions \( \phi \approx 21\% \) and \( \phi \approx 42\% \), respectively). The agreement is good for both densities, with RISM able to predict the structuring of the \( S_{ij}(k) \) as the density increases. The main peak at \( k\sigma \approx 6.5, \) clearly visible at \( \rho^* = 0.4 \) suggests a geometrical arrangement in which two dumbbells are closely packed, with each sphere of a dumbbell linked in a close configuration with the spheres of another dumbbell. This geometry is compatible with the relatively high value of the packing fraction and constantly emerges in the site-site correlations of all models.

On the other hand, since the structuring of \( S_{ij}(k) \) is exclusively driven by packing effects, the related features tend to vanish when the density decreases: at \( \rho^* = 0.2 \) only a small shoulder in \( S_{ij}(k) \) is visible, reminiscent of the well defined peak observed at \( \rho^* = 0.4 \).

A different behavior is expected for the SW-SW fluid; in particular, due to the isotropy of both molecular geometry and interaction potential, we expect a standard gas-liquid phase separation to take place below a certain critical temperature. Indeed, as visible from Fig. 3a, at high temperature (\( T^* = 0.70 \)), the behavior of \( S_{ij}(k) \) closely resembles the HS-HS situation, especially at high density. Then, as the temperature is lowered, the \( k \to 0 \) limit of \( S_{ij}(k) \) remarkably increases at \( \rho^* = 0.2 \) (see Fig. 3b), signaling a possible approach to a gas-liquid phase separation, as we shall further comment below. Such a feature disappears at high density, because packing effects tend to suppress density fluctuations on a large-distance scale. Also for the SW-SW model, predictions faithfully reproduce MC results by proving able, in particular, to follow the observed increase of \( S_{ij}(k \to 0) \).

A third physical scenario is observed for the HS-SW fluid. Site-site structure factors at different temperatures (\( T^* = 0.55 \) and 0.30) and densities (\( \rho^* = 0.20 \) and 0.40)
are reported in Fig. 4 where, due to the different interaction sites, three site-site structure factors are explicitly displayed. The presence of only one attractive interaction (positioned on site 2 of the dumbbell) has a deep influence on the structure of the fluid: in all panels of Fig. 4 we observe the presence and progressive enhancement of a low-
$k$ peak in $S_{22}(k)$, at $k\sigma \sim 2$ — beside the main correlation peak at $k\sigma \sim 6.5$ — and the simultaneous absence of any diverging trend in the $k \to 0$ limit of all $S_{ij}(k)$. This evidence is compatible with a physical picture in which dumbbells tend to self-aggregate, forming clusters out of the homogeneous fluid as the temperature decreases. Indeed it has been shown that the development of a low-
$k$ peak in $S_{22}(k)$ is correlated to the formation of aggregates both experimentally, as for instance in colloid-polymer mixtures and globular protein solutions (see e.g. [70, 71]), as well as in theoretical and numerical investigations of model fluid with microscopic competing interactions (see e.g. [72, 73] and references). Recently, such a feature in the structure factor has been more generally related to the presence of some kind of “intermediate-range order” in the fluid [74, 75]. In our case, the presence of stable clusters clearly emerges also by visual inspection of the equilibrated MC configurations (see next Fig. 12). Also in this case, RISM positively predicts all structural features, and in particular the progressive enhancement of the low-
$k$ peak: only at low temperature and density (see Fig. 4c), RISM yields a less structured $S_{22}(k)$ in comparison with the MC datum. This can be explained by the difficulty the RISM faces to reproduce the structure of a fluid that turns progressively non-homogeneous, as signaled for instance by the pronounced height of the low-
$k$ peak visible in Fig. 4c.

An interesting feature emerging from Fig. 4 — and particularly well documented in panel (d) — is the development of a pronounced negative minimum in $S_{12}(k)$ as the temperature decreases and the density increases, accompanied by the progressive alignment between such a minimum and the main peaks of $S_{11}(k)$ and $S_{22}(k)$. Such a behavior amounts to a substantially equal pace in the ordering of the HS and SW sites of the dumbbells. A similar alignment in the structure factors is known to

FIG. 4: MC (symbols) and RISM (lines) $S_{ij}(k)$ for the HS-SW fluid at different [$T^*, \rho^*$] conditions: [0.55, 0.2] (a); [0.55, 0.4] (b); [0.30, 0.2] (c); [0.30, 0.4] (d). Subscripts 1 and 2 refer to the HS and SW site, respectively.
FIG. 5: MC centre-centre structure factors for the HS-SW fluid at fixed $\rho^*=0.20$ and different temperatures.

FIG. 6: MC (symbols) and RISM (lines) internal energy per particle for the SW-SW fluid at high, intermediate and low temperatures.

We complete our structural investigation of the HS-SW fluid with Fig. 5, where we show the behavior of the molecular centre-centre structure factor, $S_{cc}(k)$, at fixed density, $\rho^*=0.20$, and various temperatures. In the figure, the development of the low-$k$ peak is visible even in the $S_{cc}(k)$, though this feature is smoother than in the corresponding $S_{22}(k)$. We report only MC results, since centre-centre correlations can be included in the RISM formalism for the two-site model at issue only at the cost of introducing a “ghost site” (i.e. bearing no interactions) to represent the centre of the molecule; we have avoided such a procedure since previous studies \cite{77} have shown that the presence of ghost sites spuriously influences the behavior of correlations involving the remaining “real” sites.

Free energy and phase equilibria

According to the procedure described in Sect. II — see Eqs. (8) and (9) — the starting point for the determination of fluid phase equilibria in the RISM formalism is the calculation of the internal energy along several isotherms. Three examples of such calculations for the SW-SW model at high, intermediate and low temperatures are reported in Fig. 6: we see that theoretical predictions are in close agreement with simulation data at $T^*=0.70$ and $T^*=0.60$, whereas small discrepancies appear at low temperature, i.e. at $T^*=0.55$. 

take place in two-component ionic fluids where alternate order of oppositely charged particles emerges, so to cope with charge neutrality constraints (see Ref. \cite{76} for a detailed illustration). In the present case, the alignment may be attributed to the combined effect of energy minimization, achieved via the clustering of SW sites, with the ensuing drag imposed to the rigidly linked HS site.

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FIG. 7: RISM free energy (a) and pressure (b) for the SW-SW fluid as functions of the density along several isotherms.
FIG. 8: Panel a: RISM (circles) and MC (squares) gas-liquid coexistence points for the SW-SW fluid; full lines are bestfits calculated according to the scaling law for the densities and the law of rectilinear diameters; the critical points obtained within this fitting procedure are indicated by crosses. Panel b: histograms of the probability $P(N)$ to find the system with $N$ particles in the simulation box for various temperatures and chemical potentials, as obtained by SUS grand-canonical simulations. The box length is 13.57\(\sigma\).

In Fig. 8, where we show that, starting from an almost homogeneous distribution at $T^*=0.527$, two well defined peaks develop upon cooling the system, corresponding to the densities of the gas and liquid phases. As visible from Fig. 8a, the RISM turns out to overestimate the gas-liquid coexistence curve, in agreement with a previous study on the same model with $\lambda=0.5$ [18], where the RISM was coupled with a Mean Spherical Approximation closure. We have calculated the RISM and MC critical temperature and density from corresponding coexistence points, through the scaling law for the densities and the law of rectilinear diameters with an effective critical exponent $\beta=0.32$ [78]. Results of such bestfit procedure, also reported in Fig. 8a, are: $T^*_c=0.598$ and $\rho^{\ast}_{c}=0.307$ for RISM, and $T^*_c=0.527$ and $\rho^{\ast}_{c}=0.221$ for MC. Notwithstanding the relative discrepancies, both RISM theory and MC simulations provide a picture of the SW-SW model as a standard isotropic fluid, thus confirming the indications coming from the structural analysis about the existence of a gas-liquid phase separation.

As far as the HS-SW model is concerned, RISM and MC results for the internal energy are reported in Fig. 9.

RISM predictions for the gas-liquid coexistence points of the SW-SW model are reported in Fig. 8a, along with corresponding MC data. As for the latter, MC distributions of densities in the $\mu VT$ ensemble are plotted in

![FIG. 9: MC (symbols) and RISM (lines) internal energy per particle for the HS-SW fluid at high, intermediate and low temperatures.](image-url)
FIG. 10: RISM free energy (a) and pressure (b) for the HS-SW fluid as functions of the density along several isotherms. All free energy curves exhibit a monotonous trend to increase, with no appreciable concavity changes all over the investigated temperature range. As a consequence, pressure does not exhibit any van der Waals loop, suggesting a supercritical behavior of the HS-SW model down to $T^\ast = 0.28$; eventually, the convergence of the RISM numerical algorithm eventually fails immediately below this temperature. Such a RISM picture is coherent with the MC observation: down to $T^\ast = 0.20$, the lowest $T$ where we have been able to equilibrate the fluid, SUS does not show any double-peak behavior in the probability density $P(N)$, ruling out the existence of a gas-liquid phase separation for $T^\ast > 0.20$. Below such a temperature MC results are not available, due to the exceedingly long computational time required to equilibrate the system.

Collecting structural and thermodynamic observations, the phase behavior of the HS-SW model is summarized in Fig. 11, where the RISM predictions for the first appearance of the low-$k$ peak in $S_{\!22}(k)$ are also reported. As visible, such predicted values form a border line separating a region in the $T - \rho$ diagram where a pure homogeneous fluid exists, at high temperatures, from another region, at lower temperatures, where a locally non-homogeneous cluster fluid takes place. We have determined such a border line within the RISM approach, since the theoretical scheme yields, as discussed in Fig. 4, accurate structural predictions in this temperature regime; moreover, RISM allows — in comparison with MC calculations — for a finer spanning of different thermodynamic conditions and for a more accurate observation of the early development of the low-$k$ peak. We note that the temperature of the first appearance of the low-$k$ peak in $S_{22}(k)$ hardly changes at low and intermediate densities, keeping an almost constant value $\sim 0.7$. Conversely, when $\rho^\ast > 0.2$ the low-$k$ peak develops at progressively higher temperatures, signaling that increasing the density promotes the formation of self-assembled structures in the system. For completeness, we also report in Fig. 11 the low-temperature regime out of operational conditions for RISM calculations.

FIG. 11: RISM predictions for the phase behavior of the HS-SW fluid (symbols). The grey area is separated from the cyan zone by a border line identified by the appearance of the low-$k$ peak in the $S_{22}(k)$. Snapshots schematically illustrate the different arrangements of the fluid across the border line with red and blue spheres indicating SW and HS sites, respectively. The underlying orange area is out of operational conditions for RISM calculations.
panel a) and high ($\rho^* = 0.40$, panel b) densities. A different scenario emerges at $T^* = 0.25$: at low density, ($\rho^* = 0.05$, panel c), isolated clusters of almost spherical shape, constituted by a variable number of dumbbells, are clearly visible, confirming the indications given by the static structure factors. A different geometrical arrangement is instead observed at high density, ($\rho^* = 0.40$, panel d), with dumbbells forming macro-domains almost spanning the simulation box.

To summarize, convergent thermodynamic and structural evidence, coming from theory and simulations, possibly suggests that in the HS-SW fluid the self-assembly process inhibits the gas-liquid phase separation, or at least shrinks it into a region of the phase diagram small enough to be inaccessible to both RISM and MC. To further elucidate this point, we have studied the phase behavior of several models, intermediate between the SW-SW and the HS-SW ones. Specifically, we have calculated the critical points of SW-SW models in which the square-well depth of site 1, $\epsilon_1$, is progressively turned from one to zero. In this way, the case $\epsilon_1 = 1$ corresponds to the original SW-SW model whereas, at the opposite limit, $\epsilon_1 = 0$ we recover the HS-SW model. In Fig. 13 we show the RISM and MC critical temperatures as functions of $\epsilon_1$: remarkably, the two sets of data lie on almost parallel straight lines, with a constant discrepancy of $\sim 0.06$ in the predicted values of $T^*_{\text{crit}}$. Numerical values of MC and RISM critical parameters are reported in Tab. I along with the relative error bars. By comparing the trends of $T^*_{\text{crit}}$ and $\rho^*_{\text{crit}}$, both RISM and MC document that $T^*_{\text{crit}}$ decreases upon lowering $\epsilon_1$, whereas $\rho^*_{\text{crit}}$ keeps generally constant almost independently on the specific value of $\epsilon_1$. Extrapolating to $\epsilon_1 = 0$, we obtain for the putative critical temperature of the HS-SW model $T^*_{\text{crit}} \sim 0.16$ and $\sim 0.10$ from RISM and MC, respectively. Such values are out of the operational range of both integral equa-
FIG. 13: RISM (circles) and MC (squares) critical temperatures of intermediate SW-SW models with variable $\epsilon_1$. Lines are linear fits of calculated points.

CONCLUSIONS

We have investigated by RISM/HNC integral equation theory and MC simulations the structural and thermodynamic properties of different colloidal dumbbells. Specifically, we have studied a model composed by two identical tangent hard spheres surrounded by two identical short-range square-well interactions (SW-SW model), and a second model in which only one square-well interaction is present (HS-SW model). We have also characterized the phase behavior of a series of intermediate models, by progressively reducing to zero the square-well depth on one of the two sites of the SW-SW model, and, for completeness, also the structural properties of the tangent homonuclear hard dumbbell fluid.

We have analyzed the phase behavior and gas-liquid equilibria by employing the energy route from structure to thermodynamics in the RISM framework; other schemes, like the compressibility route and the HNC closed formulae turn to be less reliable in our case. As for the simulation approach, we have carried out successive umbrella sampling calculations to obtain the pressure and chemical potential. RISM and MC agree in documenting two completely different physical scenarios for the SW-SW and HS-SW models. As for the former, we have found a standard gas-liquid coexistence curve, with the RISM theory slightly overestimating the critical temperature and density in comparison with simulation data. MC structure factors are well reproduced by RISM, suggesting that the isothermal compressibility is generally well predicted. As for the HS-SW model, the appearance and growth of a low-$k$ peak in the static structure factor signal the development of a locally non-homogeneous cluster fluid. At low temperatures the formation of such aggregates plausibly inhibits the gas-liquid phase separation and gives rise to a fluid constituted by well defined, essentially non-interacting clusters. RISM and MC calculations concerning the intermediate models between SW-SW and HS-SW show a linear decrease of the critical temperature as a function of the square-well depth. A straightforward extrapolation of such data predicts that, should a critical temperature exist for the HS-SW model, it would be low enough to fall out of RISM and MC operational ranges.

The models investigated in this work exhibit a rich phase behavior, including the presence of phase separation and self-assembly processes. Such models are characterized by a relative simple design and we have documented how reliable predictions concerning their structural and thermodynamic properties can be obtained within the RISM theoretical framework. Such desirable and advantageous properties set the SW-SW, HS-SW and intermediate models as ideal candidates to elucidate

TABLE I: Critical parameters for the SW-SW models with variable $\epsilon_1$. RISM and MC error bars correspond to the uncertainties by which we have appreciated the development, respectively, of a van der Waals loop in the pressure (see Fig. 7b) and of a double peak in the P(N) (see Fig. 8b).

| $\epsilon_1$ | $T^*$ | $\rho^*$ | $\mu/\epsilon$ |
|-------------|-------|---------|---------------|
| 1.0         | 0.527±0.001 | 0.22±0.01 | -1.813       |
| 0.7         | 0.408±0.002 | 0.21±0.01 | -1.453       |
| 0.5         | 0.328±0.003 | 0.19±0.02 | -1.377       |
| 0.4         | 0.275±0.005 | 0.23±0.01 | -1.729       |
| 0.2         | 0.190±0.010 | 0.22±0.02 | -2.055       |

| $\epsilon_1$ | $T^*$ | $\rho^*$ | $\mu/\epsilon$ |
|-------------|-------|---------|---------------|
| 1.0         | 0.60±0.01  | 0.31±0.05 | -1.476       |
| 0.7         | 0.47±0.01  | 0.30±0.05 | -1.128       |
| 0.5         | 0.38±0.01  | 0.29±0.05 | -1.063       |
| 0.4         | 0.33±0.01  | 0.30±0.05 | -1.127       |
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