Complex Phase Behavior of The System of Particles with Smooth Potential with Repulsive Shoulder and Attractive Well

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We report a detailed simulation study of the phase behavior of core softened system with attractive well. Different repulsive shoulder widths and attractive well depths are considered which allows to monitor the influence of repulsive and attractive forces on the phase diagram of the system. Thermodynamic anomalies in the systems are also studied. It is shown that the diffusion anomaly is stabilized by small attraction.

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I. INTRODUCTION

In 1970-th Hemmer and Stell introduced a model system which can effectively approximate real substances \[ \sigma < r < \sigma \] \[ \infty \] \[ \varepsilon \] \[ \rho \] \[ \varepsilon \] \[ \rho \] \[ \varepsilon \] \[ \rho \]. The model they introduced belongs to the class of potentials which nowadays is called core-softened potentials, i.e. the system with softening of the repulsive part of interparticle interaction. Hemmer and Stell showed that such systems can demonstrate some unusual phase transitions - transition between two crystal phases of the same symmetry \[ \sigma \] \[ \infty \] \[ \varepsilon \] \[ \rho \] \[ \varepsilon \] \[ \rho \]. which ends in a critical point similar to the gas-liquid one, and liquid - liquid phase transition. In Ref. \[ \sigma \] \[ \infty \] \[ \varepsilon \] \[ \rho \] it was proposed that the high density transition with critical point qualitatively represents the isostructural transition in Cs and Ce.

Great interest to this kind of systems appeared after Hemmer and Stell publications. Many researchers studied this model or proposed other core-softened model potentials.

Young and Alder carried out simulation of collapsing spheres (CS) system which is defined as \[ U(r) = \infty \] if \[ \sigma < r \], \[ U(r) = \varepsilon \] if \[ \sigma < r < \sigma_1 \] and \[ U(r) = 0 \] otherwise \[ \sigma \] \[ \infty \] \[ \varepsilon \] \[ \rho \]. Because of the computer power restrictions they managed to estimate the melting line of the system only in two-dimensional case. According to their’s results the melting line demonstrates a maximum. They pointed out the similarity of the phase diagrams of the collapsing spheres system and experimental phase diagram of Ce and Cs.

However, Young and Alder did not consider solid-solid phase transformation of collapsing spheres. This was done by Bolhuis and Frenkel who studied the CS system by Monte-Carlo simulation \[ \sigma \] \[ \infty \] \[ \varepsilon \] \[ \rho \]. They considered isostructural FCC-FCC transition in the collapsing spheres and square well systems. As it was shown in the cited paper, the isostructural transition takes place in both systems for sufficiently small soft core or square well widths. If the width of the soft core (well) increases the solid-solid transition disappears.

Velasco et al. studied the collapsing spheres system in the frame of thermodynamic perturbation theory \[ \sigma \]. Their’s results are in good agreement with the Bolhuis and Frenkel publication \[ \sigma \]. They considered four values of the step width: \[ \sigma_1 = 1.03; 1.08; 1.1 \] and \[ 1.16 \]. According to their’s findings the first three systems demonstrate the isostructural solid-solid transformation with critical point while the last system does not have this transition. At the same time an FCC-BCC-FCC sequence occurs in the system with the largest step size.

The qualitative phase behavior of collapsing spheres was studied by Stishov \[ \sigma \]. This article makes a qualitative estimation of the collapsing spheres phase diagram basing on the high- and low- temperature limits. It was shown that depending on the \[ \sigma_1/\sigma \] ratio the phase diagram can change dramatically. This qualitative consideration is in good agreement with Monte-Carlo simulation \[ \sigma \] and perturbation theory results \[ \sigma \] mentioned above. In Refs. \[ \sigma \] \[ 10 \] it was discussed the possibility of the liquid-liquid phase transition in CS system.

One can use the geometrical reasons to identify the possible structures of the core softened systems. This method was applied by Jagla to a set of systems \[ \sigma \]. In this paper a parameter dependent potential was considered. Depending on the value of the tuning parameter it can be continuously changed from a hard core plus linear ramp shape to hard core plus repulsive shoulder one. The minimal energy configurations corresponding to different pressures for the different potentials were monitored. It was established that depending on the pressure the number of overlaps of the soft core changes producing a large number of possible geometrical configurations (Fig. 3 in \[ \sigma \]). Basing on this argument one can expect a rich variety of structures in the core softened systems both in crystalline and disordered regions.

Although the main focus of Ref. \[ \sigma \] was on two-dimensional systems, the results were also generalized for three-dimensional case (Fig. 6 in \[ \sigma \]). These results clearly state that the crystalline region of the linear ramp system demonstrates many phases with different symmetry. This fact identifies that core-softening is a very strong mechanism affecting the phase behavior of the system.

The minimum energy configurations in the two-
dimensional collapsing spheres system was revised later in Refs. \[12, 13\]. In this paper the MC simulation of the system was also carried out and complex phase behavior in liquid phase was observed. Depending on the density, the system can form different cluster phases. In particular, long stripe clusters were observed at some densities and temperatures.

The same system of two-dimensional collapsing spheres was studied further in Ref. \[14\]. The stripe phases for a set of the step widths were observed. The authors pointed out that the stripe phase takes place only for some particular values of the step width. Although the paper was mainly focused on the two-dimensional system the authors claim that the conclusions are applicable for the three dimensional case too.

Another soft core softened model in two dimensions was considered by Camp \[15, 16\]. Phase diagram obtained from NPT-MC was reported. This phase diagram consists from low- and high density solid phases, normal liquid and cluster liquid. The cluster liquid represents the stripe phase.

Interestingly, the stripe phases were observed experimentally in the system of colloids in magnetic field \[17\]. The configurations observed in this system closely resemble the ones obtained by Camp \[15\]. This justifies that the core-softened models can be successfully applied to the real experimental systems.

A strong method of the ground state phase calculation was developed in Refs. \[18, 19\]. This method allows to find the minimal energy configurations by applying generic algorithms carrying out the minimization. The collapsing sphere system with different step widths was considered in Refs. \[18, 19\]. Three values of the step were considered: $\sigma_1 = 1.5$, $\sigma_1 = 4.5$ and $\sigma_1 = 10.0$. It was shown that the complexity of the system increases dramatically with increasing the step size. For example, for the system with $\sigma_1 = 1.5$ the number of phases reported in \[18\] is 6, for $\sigma_1 = 4.5 - 33$ and for $\sigma_1 = 10.0 - 47$.

In our recent paper a smoothed repulsive shoulder system (RSS) was introduced \[20\]. This model is defined by the interparticle potential

$$U(r) = \left(\frac{\sigma_0}{r}\right)^{14} + \frac{1}{2}\varepsilon(1 - \tanh(k_0[r - \sigma_1])), $$

where $k_0 = 10.0$ and the step width $\sigma_1$ was varied. The dependence of the phase diagram on $\sigma_1$ was studied. The following values of $\sigma_1$ were considered: 1.15, 1.35, 1.55 (Ref. \[20\]) and 1.80 (Ref. \[21\]). In agreement with previous discussion, the behavior of the system was found to be very complex.

If the step width is relatively small then the crystalline region consists of low- and high density FCC phases separated by a BCC region. However, already at $\sigma_1 = 1.35$ the complexity of the phase diagram greatly increases. It is important to note that several crystalline structures appear in the system including not close packed structures which cannot be observed in LJ-like systems. Comparing the phase diagrams for $\sigma_1 = 1.35$, 1.55 and 1.8, one can see that the complexity of the phase diagram even increases with increasing the step width.

Later the ground state of the RSS with $\sigma_1 = 1.35$ was studied in the work \[22\]. The set of the phases reported in this work is different from the one in \[20\]. It can be related to the different choice of the phases the authors of these papers considered to be potentially stable.

One can see that the behavior of the purely repulsive core-softened models is rather complex. However, the potentials of interaction between real particles have both repulsive and attractive parts. To take it into account one should add an attractive well to the repulsive core-softened model. The potentials of this type were reported as models of water, liquid metals, colloidal particles or polymer colloid mixtures and so on. This makes them important for the soft matter science and attracts much attention to such systems.

The simplest core-softened system with attraction is the collapsing spheres system with additional attractive well (CSAW):

$$\Phi(r) = \begin{cases} 
\infty, & r \leq \sigma_0 \\
\varepsilon_1, & \sigma_0 < r \leq \sigma_1 \\
-\varepsilon_2, & \sigma_1 < r \leq \sigma_2 \\
0, & r > \sigma_2 
\end{cases}$$  \hspace{1cm} (1)$$

Liquid-liquid phase transition (LLPT) was found in such systems. LLPT in CSAW systems was intensively studied by molecular dynamics, integral equations theory and perturbation theory \[24–29\]. It was found that LLPT takes place only at some specific values of parameters $\varepsilon_2/\varepsilon_1$, $\sigma_1/\sigma_0$ and $\sigma_2/\sigma_0$. However, as far as we know, all papers on this topic suggest that LLPT is metastable with respect to crystallization. This makes extremely important to know also the melting line of the system. However, just a few publications consider the crystalline region of the phase diagram \[30, 31\].

In the paper \[32\] the LLPT in CSAW was studied. The authors also investigated possible crystal structures in the system. They came to the conclusion that only one crystal phase is possible in the range of densities they considered. Taking into account huge variety of phases in the purely repulsive systems this conclusion looks rather surprising and makes it necessary to carry out further investigations of the influence of repulsive and attractive forces on the phase diagram of a model system.

A detailed study of the phase diagrams of a family of core-softened systems with attractive well was carried out by Quigley and Probert \[30, 31\]. The potential used in their works consisted of Lennard-Jones part plus a gaussian well. Choosing different parameters they changed the depth of the well and monitored the changes in the phase diagram. It was shown that FCC is not the only
stable crystal structure for this kind of potentials. Simple hexagonal structure was also reported [30, 31].

The goal of this paper is to provide a detailed study of the influence of attractive and repulsive forces on the phase diagram of a core-softened system. For doing this we carry out the calculations of the phase diagrams of a set of systems which have the same functional form of the interatomic potential but parameters of this potential are different. In the present article we focus on the melting line of the system and the transformations between different crystal phases. We also consider the influence of attraction on the thermodynamic anomalies in the core softened system.

### II. SYSTEM AND METHODS

In the present study a system of particles interacting via the potential with "hard" core, repulsive shoulder and attractive well is investigated. This potential represents a generalization of our previous RSS model [20, 21] and we call it repulsive shoulder system with attractive well (RSS-AW) potential.

The general form of the potential is written as

\[ U(r) = \varepsilon (\frac{\sigma}{r})^{14} + \lambda_0 - \lambda_1 \tanh(k_1(r-\sigma_1)) + \lambda_2 \tanh(k_2(r-\sigma_2)) \]

(2)

Two sets of systems are considered: the ones with the step width equal to \( \sigma_1 = 1.15 \) and the ones with the step \( \sigma_1 = 1.35 \). The parameters \( k_1 = k_2 = 10.0 \) are fixed while parameters \( \sigma_1, \sigma_2, \lambda_0, \lambda_1 \) and \( \lambda_2 \) are varied to get the different potential shape. Seven sets of parameter are considered. They are summarized in Table 1. Figs. 1 and 2 show the potentials for the step width \( \sigma_1 = 1.15 \) and \( \sigma_1 = 1.35 \) respectively. The parameters are chosen in such a way that the depth of attractive well becomes larger (see Table 1 and Figs. 1 and 2). Below we denote the systems with different parameters as system 1, system 2 and so on in accordance with Table 1.

In our previous publications [20, 21] we discussed the phase diagrams of several purely repulsive systems, i.e. the systems with zero well depth. The complexity of these phase diagrams was shown. Here we extend this study to the systems with attractive well and study the evolution of the system behavior with increasing attraction.

In order to get a hint about the possible crystal phases in the systems we measure the energies of ideal crystal lattices which correspond to zero temperature free energies. After that we simulate the most preferable

| number | \( \sigma_1 \) | \( \sigma_2 \) | \( \lambda_0 \) | \( \lambda_1 \) | \( \lambda_2 \) | well depth |
|--------|-------------|-------------|-------------|-------------|-------------|------------|
| 1      | 1.15        | 0           | 0.50        | 0           | 0           | 0          |
| 2      | 1.15        | 1.35        | 0.2         | 0.5         | 0.3         | 0.4        |
| 3      | 1.15        | 1.35        | 0.07        | 0.5         | 0.43        | 0.60       |
| 4      | 1.35        | 0           | 0.5         | 0           | 0           | 0          |
| 5      | 1.35        | 1.80        | 0.5         | 0.60        | 0.10        | 0.20       |
| 6      | 1.35        | 1.80        | 0.5         | 0.66        | 0.16        | 0.30       |
| 7      | 1.35        | 1.80        | 0.5         | 0.7         | 0.20        | 0.4        |

TABLE I: The potential parameters used in simulations (Eq. (2)).
structures at finite temperature and monitor the limits of their stability by looking at the radial distribution functions. This procedure allows to find the approximate regions of the thermodynamic parameters for free energy computations which are necessary for the exact determination of the transition lines.

We simulate the system in $NVT$ ensemble using Monte-Carlo method. The number of particles in the liquid or gas state simulation was set to 500 or 1000 and for crystal phases it varied between 500 and 1000 depending on the structure. The system was equilibrated for $10^5$ MC step and the data were collected during $10^6$ MC steps.

In order to find the transition points we carry out the free energy calculations for different phases and construct a common tangent to them. In our previous article where we considered the purely repulsive potentials we computed the free energy of the liquid by integrating the equation of state along an isotherm [35]:

$$F(T) = \int_0^{\rho} \frac{P(\rho')}{\rho'^2} d\rho'.$$

In the case of potentials which contain an attractive part the situation is more complicated because of the possible gas - liquid transition. In order to avoid the difficulties connected to this transition we carry out calculation of free energies at high temperature above the gas - liquid critical point and then calculate the free energies by integrating the internal energies along an isochore [35]

$$F(T) = \int_0^{\rho} U(T, N, V) d\rho.$$ 

Free energies of different crystal phases were determined by the method of coupling to the Einstein crystal [35].

To improve the statistics (and to check for internal consistency) the free energy of the solid was computed at many dozens of different state points and fitted to multinomial function. The fitting function we used is $a_p q T^p V^q$, where $T$ and $V = 1/\rho$ are the temperature and specific volume and powers $p$ and $q$ are related through $p + q \leq N$. The value $N$ we used for the most of calculations is 5.

In this paper we use the dimensionless quantities: $\tilde{r} = r/\sigma$, $\tilde{P} = P\sigma^3/\varepsilon$, $\tilde{V} = V/N\sigma^3 = 1/\tilde{\rho}$, $\tilde{T} = k_B T/\varepsilon$. Since we use only these reduced units we omit the tilde marks.

III. PHASE DIAGRAMS

$\sigma_1 = 1.15$ (potentials 1 - 3)

In this section we consider the phase diagrams of the systems with step width equal to $\sigma_1 = 1.15$ and different depths of the attractive well (systems 1 – 3 from Table 1). These phase diagrams are shown in Figs. 3(a) - (c) and 4(a) - (c). In our previous publication [20] we reported the phase diagrams for the purely repulsive potential (zero well depth). Figs. 3(a) and 4(a) show these phase diagrams for the sake of comparison. As one can see from these figures, the phase diagram consists from liquid and three crystalline regions: low density FCC (ld-FCC), BCC and high density FCC (hd-FCC). Note that the shoulder $\sigma_1 = 1.15$ gives relatively small perturbation to the soft spheres potential $\Phi_0(r) = \varepsilon (r/\sigma)^1$ with $n = 14$. As it was established in [35] soft spheres freeze into BCC crystal if $n < 6$ and to FCC solid if $n > 6$. It means that the shoulder makes the potential effectively more "soft".

Figs. 3(b) and 4(b) show the phase diagrams for the system 2, i.e. the system with $\sigma_1 = 1.15$ and the well depth $w = 0.4$. As it follows from the figures, the phase diagram is very similar. It again contains liquid region and three crystalline phases: ld-FCC, BCC and hd-FCC. One can see that the crystalline region shifts to the higher temperatures comparing to the previous case. This is clearly connected to the attractive forces which make the crystal phases more stable.

The phase diagram for the system 3 is shown in Figs. 3(c) and 4(c). Here the attractive well is even deeper. It leads to further increase of stability of the crystalline phases. The melting line shifts to even higher temperatures. However, the general view of the phase diagram remains the same.

Fig. 5 demonstrates all three phase diagrams in the same plot for the sake of comparison. Only $P - T$ phase diagrams are shown since $P - T$ plot would be overfilled by the data points. We observe several trends in the phase diagram evolution with increasing of the well depth. First of all, in the systems with attraction the ld-FCC phase is stable already at zero pressure while in the purely repulsive system positive pressure is necessary to stabilize the crystal. Secondly the stability of the crystalline regions with respect to melting grows with increasing the attractive well: melting temperature at the same density (or pressure) becomes higher as the attractive well becomes deeper.

The main conclusion of this section is that in the case of the potentials 1 – 3 the attractive well shifts the phase diagram, but it does not change its general shape.

$\sigma_1 = 1.35$ (potentials 4 - 7)

Now we turn to the potentials with larger width of the repulsive step $\sigma_1 = 1.35$. The phase diagram for the purely repulsive potential with $\sigma_1 = 1.35$ (potential 4) was published in our previous paper [20]. After that the zero temperature phase diagram of this system was reconsidered in the work [22]. Comparison of our phase diagram (Ref. [20]) and the zero temperature diagram from Ref. [22] shows some differences. Body-centered orthorombic (BCO), body-centered tetrahedral (BCT) and $\beta - Sn$ structures were reported to be stable into the region where we find face-centered tetrahedral (FCT) and simple cubic (SC) structures both at zero and finite
FIG. 3: (Color online) Phase diagrams of the systems with $\sigma_1 = 1.15$ (system 1 - 3) in $\rho - T$ coordinates. a - system 1, b - system 2, c - system 3.

FIG. 4: (Color online) Phase diagrams of the systems with $\sigma_1 = 1.15$ (system 1 - 3) in $P - T$ coordinates. a - system 1, b - system 2, c - system 3.
temperature. Accordingly to our results FCT and SC phases are more stable than BCO and BCT in this region. $\beta - Sn$ was not considered in our work. At the same time basing on the Ref. [22] we find that simple hexagonal (SH) structure is stable in a certain range of densities. We carry out the free energy calculations for SH crystal and add the SH transition lines into the phase diagram (Figs. 6 (a) - (b)).

The shape of this phase diagram can be intuitively explained as follows. Since the potential is purely repulsive the overlap of both hard and soft cores is energetically unfavorable. It leads to the occurrence of the close packed structure at low densities (ld-FCC). However, when the pressure (or equivalently density) increases the particles penetrate the soft core. But since this core is repulsive, this penetration is energetically unfavorable and therefore the system forms a set of structures with low coordination number - FCT (4 nearest neighbors), SC (6 nearest neighbors) and SH (8 nearest neighbors). Finally, the high density FCC (hd-FCC) crystal becomes stable which corresponds to the soft sphere limit.

Taking this into account, one can expect that the ld-FCC phase should become more stable if the potential has also an attractive part in addition to the repulsive soft core. One can also expect that ld-FCC phase occurs at lower pressures comparable to the purely repulsive potential which corresponds to the arrangement of particles in the attractive well.

Figs. 6(a) - (b) show the phase diagram for the system 5, which corresponds to the well depth $w = 0.2$.

Comparing the Figs. 5 and 6 one can see that the ld-FCC phase do become more stable. While for the purely repulsive system the maximum temperature of ld-FCC phase is $T_{\text{max},4} = 0.19$, for the system with attraction (system 5) the maximum temperature is $T_{\text{max},5} = 0.27$. At the same time the region of stability of ld-FCC phase extends and goes into the negative pressure region.

The FCT phase becomes stable in a wider density range. As a result the disordered gap presented in the system 4 phase diagram (Figs. 6(a) - (b)) is filled by the FCT crystal.

Another change in the phase diagram when the attraction is added is that the SC crystal disappears. The
FIG. 7: (Color online) Phase diagram of the system 5 (Table 1) in (a) $\rho - T$ and (b) $P - T$ coordinates.

region of SC crystal is now filled by FCT phase. The region of the SH phase is almost the same as in the case of small attraction.

In order to trace the influence of the attraction on the phase diagram we consider the systems with deeper wells - $w = 0.3$ (system 6) and $w = 0.4$ (system 7). The phase diagrams of the system 6 are presented in the Figs. 8(a) and 8(b).

One can see from Figs. 8(a) - (b) that the FCT phase goes to the lower temperatures region. Also a gap between FCT and SH crystals appears again. One observes the triple point ld-FCC - FCT - Liquid at $T = 0.11$, but at lower temperatures the transition ld-FCC - FCT disappears. One can guess that FCT is not the most thermodynamically stable phase for this system. It means that if one finds a more stable phase all these contradictions will be solved. It gives the reasons to suggest that the larger attraction makes the system to form more complex crystal phases. The identification of these phases can be a very difficult task and goes beyond the scope of the present publication.

The ld-FCC phase almost does not change. The maximum on the melting line stays the same as in the previous case (potential 6).

The range of pressures where SH structure is stable
FIG. 9: (Color online) Phase diagram of the system 7 (Table 1) in (a) $\rho - T$ and (b) $P - T$ coordinates.

almost does not change again. This structure shows very weak dependence on the attraction.

Figs. 9 (a) - (b) show the phase diagram of the system with well depth $w = 0.4$ (system 7). One can see from the figures that FCT phase disappears for this potential. The pressure range of the ld-FCC and SH structures stay almost unchanged. At the same time the HD-FCC phase moves to the lower pressures region which makes the region of SH phase stability more narrow. Interestingly the SH melting line looses the maximum observed for the previous systems. One can guess that this maximum goes under the HD-FCC melting line and becomes metastable. As a result, since SH phase does not reach its maximum, the temperature range of stability of this structure slightly decreases - from $T_{\text{sh,max,6}} = 0.38$ to $T_{\text{sh,max,7}} = 0.32$. One can expect that, if the attraction becomes even stronger, the SH phase goes into the HD-FCC region and becomes metastable with respect to it. A large gap between ld-FCC and SH phases occurs. Most probably this gap is filled by some unknown structure as it was discussed above for the system 6.

It is worth to trace the evolution of the ld- and HD-FCC phases with increasing attraction. From Figs. 10 (a) - (b) one can see that when the attraction is added the ld-FCC phase becomes more stable with respect to temperature. However, increasing of the attraction does not stabilize the ld-FCC phase any more. At the same time the attraction moves the region of ld-FCC stability to the negative pressures. One can imagine that with further increase of attractive part the melting line will have negative slope even at zero pressure which qualitatively corresponds to the case of water.

Attraction has much stronger effect on the HD-FCC melting line (Fig. 11 (a) - (b)). Small attraction ($w = 0.2$, system 5) almost does not affect the HD-FCC melting line, while increasing of the attraction moves it to the lower pressures. It makes the gap between ld-FCC and HD-FCC narrower. One can expect that at some value of the well depth the gap disappears and the crystal region of the phase diagram consists from two FCC phases only.

Fig. 12 shows the specific volume jump over the crystal phase volume at HD-FCC melting for the systems 4 – 7. Interestingly, the volume jump increases considerably with increasing the attractive well and reaches the value up to $\approx 33\%$. Experimental volume jumps are usually of the order of 5 - 10\%, although for some substances it can reach much higher values.

The example of the volume jump clearly shows the importance of the parameter $\sigma_2/\sigma_1$, where $\sigma_1$ is the step height and $\sigma_2$ - well depth. Even at the same length parameters - $\sigma_1/\sigma$ and $\sigma_2/\sigma$ the character densities in the system can be strongly different.

IV. THERMODYNAMIC ANOMALIES

Finally we would like to discuss anomalous behavior of the core softened systems. In our previous works [20, 21, 22, 42] we showed that purely repulsive system (system 4) demonstrates diffusion and density anomalies. Here we extend this study to the RSS-AW system.

The problem of anomalous behavior of isotropic core softened system with attraction has already been discussed by several authors [39-41].

In the recent publications [39, 40] the characteristic length and energies of the interatomic potential were fixed while the softness of the potential varied. It means that the focus of these publications is slightly different comparing with the present one. The authors found...
anomalous behavior in the system they studied in a wide range of the potential parameters.

In the publication [41] the depth of attractive well is varied with all other parameters fixed. In this sense this work is very close to the present one. The deepest well considered in this work is $-1.0$ which is deeper then in our study. The main conclusion of the authors is that the anomalies shrink with increasing the well depth and finally disappear.

Figs. 10 (a)-(c) present the diffusion anomaly for the systems 4, 5 and 7. One can see from these figures that the density range of anomalous diffusion does not change on increasing the well depth. At the same time the maximum temperature of anomalous behavior increases. It means that small attraction stabilizes anomalous diffusion in the system.

In order to see the origin of the difference in the qualitative behavior of diffusion anomaly region between the present work and the publication [41] we should notice that in our case the increasing of the well depth at the same time makes the potential softer (Fig. 2). This corresponds to making the parameter $\Lambda$, which controls the slope of the potential in the works [39, 40], smaller. Accordingly to these publications the anomalous region is wider for the smaller values of this parameter. Seems that this effect is larger in our case then shrinking of the
anomalous region with increasing attraction.

More detailed discussion of the anomalous behavior of the RSS-AW systems will be given in a subsequent publication.

IV. CONCLUSIONS

The present article shows the evolution of the phase diagrams of two core-softened systems with addition of attractive forces. It is shown that the general shape of the phase diagram and the set of preferable structures is mostly defined by repulsive shoulder while attractive well just shifts the phase diagram in $\rho - T$ plane. Anomalous diffusion behavior is also considered. It is shown that the appearance of the diffusion anomaly if related to the soft-core but the small attraction stabilizes it at higher temperatures.

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[1] P. C. Hemmer and G. Stell, Phys. Rev. Lett. 24, 1284(1970).
[2] G. Stell and P. C. Hemmer, J. Chem. Phys. 56, 4274 (1972).
[3] R.I. Beecroft and C.A. Swenson, J. Chem. Solids 15, 234 (1960).
[4] D.A. Young and B.J. Alder, Phys. Rev. Lett. 38, 1213 (1977).
[5] D.A. Young and B.J. Alder, Chem. Phys. 70, 473 (1979).
[6] P. Bolhuis and D. Frenkel, J. Phys.: Condens. Matter 9, 381 (1997).
[7] E. Velasco, L. Mederos, G. Navascues, P.C. Hemmer and G. Stell, Phys. Rev. Lett. 85, 122 (2000); C. Rascon, E. Velasco, L. Mederos, G. Navascues, J. Chem. Phys. 106, 6689 (1997).
[8] S.M. Stishov, Phil. Mag. B 82, 1287 (2002).
[9] V. N. Ryzhov and S. M. Stishov, Zh. Eksp. Teor. Fiz. 122, 820 (2002) [JETP 95, 710 (2002)].
[10] V. N. Ryzhov and S. M. Stishov, Phys. Rev. E 67, 010201(R) (2003).
[11] E. A. Jagla, Journal of Chemical Physics, 110, 451 (1999).
[12] G. Malescio and G. Pellicane, Nature Materials 2, 97 (2003).
[13] G. Malescio and G. Pellicane, Phys. Rev. E 70, 021202 (2004).
[14] Y. Norizoe and T. Kawakatsu, Europhys. Lett., 72, 583 (2005).
[15] P.J. Camp, Phys. Rev. E 68, 061506 (2003).
[16] P.J. Camp Phys. Rev. E 71, 031507 (2005)
[17] N. Osterman, D. Babić, I. Poberaj, J. Dobnikar and P. Zilerl, Phys. Rev. Lett. 99, 248301 (2007)
[18] G. J. Pauschenwein and G. Kahl, J. Chem. Phys. 129, 174107 (2008)
[19] G. J. Pauschenwein and G. Kahl, Soft Matter, 4, 1396 (2008)
[20] Yu. D. Fomin, N. V. Gribova, V. N. Ryzhov, S. M. Stishov and Daan Frenkel, J. Chem. Phys., 129, 064512 (2008).
[21] N. V. Gribova, Yu. D. Fomin, Daan Frenkel, V. N. Ryzhov, Phys. Rev. E 79, 051202 (2009).
[22] S. Prestipino, F. Saija, and G. Malescio, Soft Matter, 5, 2795 (2009).
[23] Yu.D. Fomin, N.V. Ryzhov and N.V. Gribova, Phys. Rev. E 81, 061201 (2010).
[24] G. Franzese, G. Malescio, A. Skibinsky, S. V. Buldrev and H. E. Stanley, Nature 409, 692 (2001).
[25] G. Franzese, G. Malescio, A. Skibinsky, S. V. Buldrev and H. E. Stanley, Phys. Rev. E 66, 051206 (2002).
[26] M. R. Sadr-Lahijany, A. Scala, S. V. Buldrev and H. E. Stanley, Phys. Rev. Lett. 81, 4895 (1998).
[27] M. R. Sadr-Lahijany, A. Scala, S. V. Buldrev and H. E. Stanley, Phys. Rev. E 60, 6714 (1999).
[28] G. Malescio and G. Pellicane, Phys. Rev. E 63, 20501(R) (2001).
[29] Yu. D. Fomin, V. N. Ryzhov, and E. E. Tareyeva, Phys. Rev. E 74, 041201 (2006).
[30] D. Quigley and M.I.J. Probert, Phys. Rev. E 71, 065701 (2005).
[31] D. Quigley and M.I.J. Probert, Phys. Rev. E 72, 061202 (2005).
[32] G. Franzese, G. Malescio, A. Skibinsky, S. Buldrev, H. Stanley, Phys. Rev. E, 66, 051206 (2002).
[33] E.A. Jagla, Phys. Rev. E, 63, 061501 (2001).
[34] G. Malesio, G. Pellicane, Phys. Rev. E, 63, 020501 (2001).
[35] D. Frenkel, B. Smit “Understanding Molecular Simulation” Academic Press (2002).
[36] D. A. Kofke and P. G. Bolhuis, Phys. Rev. E 59, 618 (1999).
[37] G. Malesio, G. Pellicane, Phys. Rev. E, 70, 021201 (2004).
[38] Rupal Agrawal and David A. Kofke Phys. Rev. Lett. 74, 122 (1995).
[39] P. Vilaseca, G. Franzese, arXiv:1004.3186
[40] P. Vilaseca, G. Franzese, arXiv:1005.1041
[41] J. Nunes da Silva, E. Salcedo, A. B. de Oliveira, M. C. Barbosa, arXiv:1006.0033
[42] Yu.D. Fomin, V.N. Ryzhov, arXiv:1008.0039