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Range effect on percolation threshold and structural properties for short-range attractive spheres

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Percolation or aggregation in colloidal system is important in many fields of science and technology. Using molecular dynamics simulations, we study the percolation behavior for systems consisting of spheres interacting with short-range square-well (SRSW) which mimic colloidal particles, with different interaction ranges. We specifically focus on how the interaction range affects the percolation thresholds in the supercritical region. We find that the contact percolation boundaries are strongly dependent on the interaction ranges of SRSW, especially away from the liquid-liquid critical point. However, varying the interaction ranges of SRSW does not affect much the structure along percolation boundaries especially for low packing fractions. For instance, along the percolation boundary, distributions of coordination number show convergence, and distributions of cluster size are universal for different interaction ranges considered. In addition, either the bond percolation boundaries or isolines of average bond coordination number collapse to those for Baxter sticky model on phase diagram, which confirms the extended law of corresponding states. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4906084]

I. INTRODUCTION

Percolation has long been studied in the past few decades,^{1–12} and percolation theory has been widely applied to the analysis of the aggregation behavior of small particles, such as colloids, spherical proteins, and micelles.^{13–20} The percolation threshold (PT) refers to the point at which colloidal particles aggregate to form an infinite cluster that spans the suspension. Such phase transition dramatically alters the original structure of the system, leading to changes in bulk conductivity^{21,22} and mechanical property.^{23,24} In addition, inside the percolated regime, when the system is further compressed or quenched, dynamical arrest and gelation of colloidal particles could occur.^{13,16–18,25–27} Thus, in-depth research on percolation in colloidal system is of great significance in many fields of science and technology.

It is widely assumed that percolation follows the concept of scaling. However, according to recent study,⁸ whether the probability of percolation exhibits scaling depends on the spanning rule.⁸ In fact, Skvor *et al.*^{8,10,11} determined the PTs of fluids with short-range interaction. They found that only the wrapping probability of percolation can be described by universal scaling functions, which enables the estimation of PT in fluid in general. Using the same criteria as above, Neitsch *et al.*¹² determined the PTs of square-well fluids and obtained the universality of the critical exponents.

The scaling behavior described above is mainly for models with short-range interaction showing metastable liquid-liquid critical point (LLCP) and liquid-liquid phase separation line. Short-ranged attractions^{6–10,28} between colloidal particles are commonly used to describe interactions such as hydrophobic effect, van der Waals force, or surface chemical bonding.²⁸ The loci of the LLCP and phase separation line are very sensitive to the attractive range between particles,^{29–32} yet how the attractive range affects the loci of PTs is not much investigated. Therefore, determining the PTs with different interaction ranges is of great interest. In addition, we will discuss how distributions of coordination number and cluster size change near PT. Particularly, we focus on intermediate volume fractions, where percolation transition often takes place. To avoid the interruption of phase separation and crystallization, we limit our discussion to the percolation transition and relevant structural transformation in supercritical state.

Molecular dynamics (MD) simulation was implemented in previous researches on spherical colloids.^{9,14,20,33–39} In our study, due to its advantages in dealing with discretized potentials, the event-driven MD⁴⁰ is employed to determine the loci of PTs for two types of percolation (namely, contact percolation and bond percolation, see Sec. II) and to investigate the structural properties of the colloidal system. We find that the PTs for contact percolation are strongly dependent on the range of the inter-particle interactions, particularly in the region away from the LLCP. However, PTs for bond percolation with different interaction ranges collapse to the PT for Baxter sticky model. The manuscript is organized as follows: Sec. II introduces the model and simulation methods.

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The determination of the PTs and the analysis of structural properties near percolation transition are presented in Sec. III. Sec. IV is the summary.

II. SIMULATION METHOD

A. The model

Colloidal particles are considered as impenetrable hardspheres devoid of internal degrees of freedom with diameter σ . According to Noro-Frenkel extended law of corresponding states,⁴¹ phase properties are insensitive to the specific shape of the interaction potential for short-range attractive system. Thus, we set the interaction between two spheres as pairwise short-range square-well (SRSW) potential,^{29–31,33–35,41,42} which serves as the basic state for understanding the role of attractions in phase transition process,

$$U(r) = \begin{cases} \infty & \text{for } r < d \\ -U_0 & \text{for } d < r < d\lambda, \\ 0 & \text{for } r > d\lambda \end{cases}$$
(1)

where U_0 is the well depth, λ controls the well width, r is the particle distance, and d represents the contacting distance. For single component system, $d = \sigma$. We note that when $\lambda \rightarrow \sigma$ and $U_0 \rightarrow \infty$, the SRSW model is the Baxter sticky model.⁴³ In our study, U_0 and σ are the units of energy and length, respectively. $T^* = k_B T / U_0$ is the reduced temperature.

For our model, the second virial coefficient, B_2 , is given as

$$B_2 = 4\pi \int_0^\infty \left[1 - \exp\left(\frac{-U(r)}{k_B T}\right) \right] r^2 dr.$$
 (2)

Combining Eq. (1) and Eq. (2), we obtain the reduced second virial coefficient, B_2^* , by

$$B_2^* = \frac{B_2}{B_{\rm HS}} = 1 - \left[\exp\left(\frac{U_0}{k_B T}\right) - 1 \right] (\lambda^3 - 1), \tag{3}$$

where $B_{\rm HS} = 4 \pi \sigma^3/3$ is the second virial coefficient of hard sphere system. According to Noro-Frenkel extended law of corresponding states,^{6,7,15,41} all systems consisting of shortrange attractive particles near LLCP are characterized by the same thermodynamic properties at the same B_2^* .

B. Simulation details

Our system consists of N mono-particles interacting with SRSW potential, contained in a cubic box of size L. Using canonical ensemble (constant number of particle, volume and temperature, NVT-ensemble), we carry out event-driven MD simulation by employing periodic boundary condition.

All the initial configurations are prepared as follows. First, N particles are uniformly distributed on FCC crystal lattice to prevent overlaps. The system is then compressed and equilibrated to reach the targeted packing fraction $\phi = \pi \sigma^3 N/6L^3$. The system is quenched to the desired temperature from high temperature ($T^* = 10$, far above the metastable liquid-liquid phase separation line on a phase diagram^{27,32}) using Andersen

thermostat. Additional long run (at least 10⁷ events) is performed to equilibrate the system. Equilibration can never be realized if the system crosses the phase separation line.⁷ We do not consider polydispersity since crystal phases barely occur within the density and temperature range of our interest.

C. Cluster and coordination number

The cluster refers to a group of particles that are connected to one another. For our model, we can either define cluster as contact cluster or bond cluster. The contact cluster refers to an ensemble of particles that are within the interaction range of each other, i.e., $r < \lambda \sigma$ for SRSW potential. The contact coordination number z of a given particle is the number of particles in contact with it. The average contact coordination number, $\langle z \rangle$, is obtained by averaging z over the system. The distribution of contact cluster size n(s) is obtained by adding up the number of contact clusters of size s. To avoid biased presentation towards small-sized clusters, here, we employ Stauffer's method¹ to normalize n(s) by

$$n_0(s) = \frac{s}{N}n(s),\tag{4}$$

where $n_0(s)$ is normalized distribution of contact cluster size.

In our study, the average contact aggregation number, $\langle s \rangle$, and the weight average contact aggregation number, $\langle s \rangle_w$, are defined as

$$\langle s \rangle \equiv \frac{\sum\limits_{s=1}^{N} s \times n(s)}{\sum\limits_{s=1}^{N} n(s)},$$
(5)

$$\langle s \rangle_w \equiv \frac{\langle s^2 \rangle}{\langle s \rangle} = \frac{\sum\limits_{s=1}^N s^2 \times n(s)}{\sum\limits_{s=1}^N s \times n(s)}.$$
 (6)

 $\langle s \rangle$ represents the average size of a randomly chosen cluster and $\langle s \rangle_w$ represents the average size of a cluster that a randomly chosen particle belongs to. We note that the numerator in Eq. (5) and the denominator in Eq. (6) actually are equal to N because $\langle s \rangle$ is equal to the total number of particles divided by total number of clusters.

An alternative way to define cluster is based on potential energy U(r). For each configuration, we construct fictitious bonds between any pairs of particles with bond probability $P(r) = 1 - \exp(U(r)/k_BT)$. Since the potential that we use is square-well interaction, particles are bonded with probability $P = 1 - \exp(-U_0/k_BT)$ only when they are within the interaction range of each other. We note that this criterion is analogous to those of Hill cluster⁴⁴ and Coniglio-Klein cluster for lattice gas model⁴⁵ with a different coefficient in the fictitious bond probability, $P_{CK}(r) = 1 - \exp(U(r)/2k_BT)$.

The bond cluster is then defined as an ensemble of particles that are linked by bonds.^{20,37,38,46} Accordingly, $z^* = P \times z$ represents the bond coordination number, and $\langle z^* \rangle = P \times \langle z \rangle$ represents the average bond coordination number of the system. By adding up the number of bond clusters of size *s*, we get the distribution of bond cluster size $n^*(s)$. We can

accordingly calculate the average bond aggregation number, $\langle s^* \rangle$, and weight average bond aggregation number, $\langle s^* \rangle_w$.

D. Determination of critical packing fraction

Among various criteria for percolation, we choose the wrapping rule, under which the finite size scaling is obeyed. According to this criterion, a cluster wraps (percolates) the system when any particle within the cluster is connected to its image in another replica.^{8,10} In our study, if the cluster that wraps the system is a contact cluster, the percolation is called contact percolation, while if a bond cluster wraps the system, it is called bond percolation. For each percolation in our study, there exists a PT, also known as the critical packing fraction, ϕ_c , which is a function of B_2^* and λ , i.e., $\phi_c(B_2^*,\lambda)$.

For fixed B_2^* and λ , the probability, Ω , of a cluster that wraps system can be written as a function of packing fraction ϕ and box size *L*, i.e., $\Omega(\phi, L)$. In thermodynamic limit, the box size approaches infinity $(L \to \infty)$, and $\Omega(\phi, L)$ evolves into a step function that jumps at $\phi = \phi_c$. For $\phi < \phi_c$, $\Omega = 0$, and for $\phi > \phi_c$, $\Omega = 1$. In finite size simulation, the probability function of percolation, $\Omega(\phi, L)$, is of the sigmoidal shape. We test at least three system sizes with N varying from 864 to 6912 for each B_2^* in the supercritical region (Fig. 1(a)). At each ϕ , the corresponding $\Omega(\phi, L)$ is obtained by calculating the ratio of percolated configurations among at least 10⁵ configurations (separated by 3×10^5 collision events) for the largest system (N = 6912) and 6×10^5 for the smallest system (N = 864). ϕ_c and the critical probability for percolation transition Ω_c are



FIG. 1. (a) The probability of percolation, Ω , as a function of packing fraction, ϕ , for systems of three different sizes at $B_2^* = 0.5$ and $\lambda = 1.01$. (b) The same as (a) for Ω as a function of the scaling variable, *x*.

obtained within error bar from the intersection of the probability curves for different N (Fig. 1(a)).

For more accurate determination of ϕ_c ,¹⁰ we use the scaling variable $x = (\phi - \phi_c) L^{1/\nu}$ (ν is the correlation length exponent), so that the percolation probability turns into a function of the single variable *x*. In this situation, all the $\Omega(\phi, L)$ curves plotted for different system sizes fall onto a single $\Omega(x)$ curve independent of system size *L*. To obtain ϕ_c , we fit the numerical results using the master function⁵

$$\Omega(x) = \frac{1}{1 + \exp(\sum_{i=0}^{5} a_i x^i)},$$
(7)

with eight fitting parameters ($\{a_i\}, \nu$, and ϕ_c). Exemplified in Fig. 1(b), the data obtained for different system sizes do fall onto a single master curve, consistent with the prediction of the scaling theory.⁵

It is interesting to note that both the probabilities of contact percolation and bond percolation follow the scaling behavior. Therefore, the method mentioned above can be employed to determine both contact PTs and bond PTs.

III. RESULT AND DISCUSSION

Since the extended law of corresponding states only works effectively for extremely short-range attractive potentials (no more than 10% of the particle size),^{32,42} we limit our study to three attraction range values, $\lambda = 1.01$, 1.03, and 1.05, without losing generality.

A. Determination of contact PT

Fig. 2(a) shows the location of contact PTs and the liquidliquid phase separation lines with different λ values. As an ideal reference to the square-well system, the exact location of the LLCP of the Baxter sticky model⁴³ has been determined by both simulation and theoretical calculations,^{15,42} based on which we obtain the LLCPs of our SRSW systems by mapping the phase diagram.^{12,42} The liquid-liquid phase separation lines with $\lambda = 1.01$ and $\lambda = 1.05$ are derived from Monte Carlo simulation.^{27,32}

For different interaction ranges, employing the definition of contact cluster and the spanning rule mentioned above, we determine the three groups of contact PTs. The loci of PTs form the percolation boundary (percolation line), which separates the phase diagram into a percolated and an unpercolated part. The contact percolation boundaries with different values of λ show dispersion (Fig. 2(a)). For instance, the percolation boundaries are more dispersed when B_2^* is larger and more converged as B_2^* decreases, consistent with the extended law of the corresponding state valid in the vicinity of the LLCP.⁴¹

In addition, at fixed B_2^* , the critical packing fraction for contact percolation can be written as a function of λ , i.e., $\phi_c(\lambda)$. As λ decreases, $\phi_c(\lambda)$ becomes larger. If the well-width gradually approaches zero (that is $U_0 \rightarrow \infty$), the contact percolation boundary of SRSW system in our study is that of Baxter sticky model,⁴³ the dotted line as shown in Fig. 2(a). We note that, at the same B_2^* , $\phi_c(\lambda = 1.01) - \phi_c(\lambda = 1.03)$ is larger than $\phi_c(\lambda = 1.03) - \phi_c(\lambda = 1.05)$, suggesting that the location of the

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FIG. 2. Phase diagram for SRSW system. (a) The contact and bond PTs, and (b) isolines $\langle z \rangle = 2$ and $\langle z^* \rangle = 2$ for different λ . Green and navy stars are phase separation lines as well as mapped LLCPs for $\lambda = 1.01$ and 1.05, respectively. Black solid lines represent contact percolation boundaries. Black dotted line in (a) is the percolation boundary for Baxter sticky model. Two groups of blue triangles in (a) are bond PTs for $\lambda = 1.01$ and 1.05. The red dashed lines in (b) represent $\langle z \rangle = 2$ isolines. Pink dotted lines with pentagon symbols in (b) are $\langle z^* \rangle = 2$ isolines for $\lambda = 1.01$ and 1.05. All lines between symbols are to guide the eye. The error bars are smaller than symbol sizes.

contact percolation boundary becomes less sensitive to the λ value with the increase of λ . In contrast, the critical probability for contact percolation Ω_c (~0.37) is independent of the value of B_2^* and λ . The correlation length exponent for contact percolation ν is also independent of the value of B_2^* , but slightly dependent on λ , e.g., $\nu = 0.97$ for $\lambda = 1.01$ and $\nu = 0.95$ for $\lambda = 1.05$.

B. Analysis of contact coordination number

The isoline for $\langle z \rangle = 2$, regarded as a good approximation of the contact percolation boundary predicted by mean field theory,^{27,47} is plotted in the phase diagram shown in Fig. 2(b). However, when B_2^* is either too large or too small, as can be seen from Fig. 2(b), the $\langle z \rangle = 2$ isoline seriously deviates from the contact percolation boundary. To test the interaction range effect on the locations of the isolines, we discuss three cases, $\lambda = 1.01$, 1.03, and 1.05. The dispersive feature of the isolines shown in Fig. 2(b) means that the distance between the isolines of different λ is positively correlated to the value of B_2^* . Similar results are observed for other $\langle z \rangle$ isolines (not shown). In all three interaction ranges considered, the contact percolation boundaries and $\langle z \rangle = 2$ isolines cross around $B_2^* = -0.2$, labeled by the horizontal dashed line.

Next, we investigate the structure changes in terms of the distribution of contact coordination number, $\Pi(z)$, at different thermodynamic state points near percolation transition. The distributions along contact percolation boundary for different



FIG. 3. (a) The distribution of contact coordination number, $\Pi(z)$, along contact percolation boundary. (b) $\Pi(z)$ of system at different packing fractions, ϕ , with $B_2^* = 0.7$. (c) $\Pi(z)$ of system at different ϕ with $B_2^* = -0.7$. The solid and the dashed lines represent $\Pi(z)$ for $\lambda = 1.05$ and $\lambda = 1.01$, respectively. See the legend for the meaning of the symbols.

 B_2^* are presented in Fig. 3(a), which are asymmetric function of *z* with maxima located at *z* = 1 or *z* = 2. For B_2^* increases from -0.7 to 0.9, $\Pi(z)$ increases for small *z* < 2 and decreases for larger *z* > 3. This indicates that the average contact coordination number, $\langle z \rangle = \sum_{z=0}^{\infty} z \times \Pi(z)$, is negatively correlated to B_2^* . Fig. 3(a) also shows that, at the same B_2^* , $\Pi(z)$ for different λ are more or less the same for negative B_2^* , but different for positive B_2^* . The difference becomes more obvious for $B_2^* > 0.5$. $\Pi(z)$ along the isoline $\langle z \rangle = 2$ for different λ are less dispersed, compared with those in Fig. 3(a) (see supplementary material).

To reveal the evolution of $\Pi(z)$ before and after percolation occurs, we investigate the behavior of $\Pi(z)$ for different ϕ with B_2^* fixed. Fig. 3(b) is the results for $B_2^* = 0.7$. The peak positions of $\Pi(z)$ increase with the increase of ϕ . In addition, $\Pi(z)$ is different for different interaction ranges, λ . The difference in $\Pi(z)$ for same ϕ but different λ becomes larger for higher packing fraction. We also study $\Pi(z)$ for B_2^* = -0.7 (Fig. 3(c)). We find that at fixed ϕ , the difference in $\Pi(z)$ for different λ is very minor, different from the case for B_2^* = 0.7. This indicates the convergence of structural properties for systems with different λ when B_2^* becomes smaller.

C. Analysis of contact cluster

Fig. 4 presents the average contact aggregation number $\langle s \rangle_w$ and the weight average contact aggregation number $\langle s \rangle_w$



FIG. 4. (a) The average contact aggregation number, $\langle s \rangle$, as a function of packing fraction, ϕ , at different B_2^* . (b) The weight average contact aggregation number, $\langle s \rangle_w$, as a function of ϕ at different B_2^* . Dotted lines indicate contact PTs at different B_2^* . Error bars provide the standard deviation after averaging at least 10⁵ configurations. All the results are obtained for $\lambda = 1.05$. See the legend for the meaning of the symbols. All lines are guides to the eyes.

for systems with $\lambda = 1.05$ at different B_2^* . Both of these quantities increase dramatically as the colloidal system becomes more compact. At different B_2^* , the value of contact PTs varies (Fig. 4, dotted lines). The values of $\langle s \rangle$ and $\langle s \rangle_w$ at contact PT are very close to their corresponding values for different B_2^* . For instance, at contact PT, the critical average contact aggregation number, $\langle s \rangle_w^c \sim 5$, and critical weight average contact the larger the value of B_2^* , the smaller the values of $\langle s \rangle_w^c$ and $\langle s \rangle_w^c$, highlighted by downward-sloping dashed lines in Fig. 4. At PT, $\langle s \rangle$ is rather small (~ 5), while $\langle s \rangle_w$ is quite large (~ 1000). This implies that the cluster size polydispersity, which is proportional to $\langle s \rangle_w/\langle s \rangle_s^{38}$ reaches its peak value.

Next, we investigate how $\langle s \rangle$ depends on the interaction range, λ . As shown in Figure 5, for fixed $B_2^* = 0.7$, $\langle s \rangle$ for $\lambda = 1.05$ and 1.01 are different. The higher the values of ϕ , the larger the discrepancy in $\langle s \rangle$ for two different λ at the same packing fraction. When the system is not percolated ($\phi < \phi_c$), similar behavior is observed in $\langle s \rangle_w$ for two different λ with the increase of ϕ (not shown). Fig. 5 also shows the results for two interaction ranges at fixed $B_2^* = -0.7$. We find that, at the same ϕ , the difference in $\langle s \rangle$ for different λ is much smaller, compared with the case for $B_2^* = 0.7$, consistent with the results in Sec. III A and Sec. III B.

Fig. 6(a) shows the normalized distribution of contact cluster size, $n_0(s)$, for different ϕ at $B_2^* = 0.7$. $n_0(s)$ decreases monotonically with cluster size *s* when the system is not percolated. Upon percolation at $\phi = 0.3$, $n_0(s)$ obeys a power law behavior.⁵ Fig. 6(b) shows $n_0(s)$ along contact percolation boundary, which collapse to the same curve, $n_0(s) \propto s^{1-\tau}$, with



FIG. 5. The average contact aggregation number, $\langle s \rangle$, as a function of packing fraction, ϕ , for $\lambda = 1.01$ and 1.05 at different B_2^* . Error bars provide the standard deviation after averaging at least 10⁵ configurations. See the legend for the meaning of the symbols. Solid and dashed lines are guides to the eyes.

 τ the Fisher exponent, $\tau = 2.08$ for $B_2^* = -0.7$, and largest $\tau = 2.17$ for $B_2^* = 0.9$. After percolation at $\phi > \phi_c$, the system then separates into a sol-like part with small-sized clusters and a gellike part with large-sized clusters (Fig. 6(a)). More discussion is provided in supplementary material.⁴⁸

D. Determination of bond PT and analysis of relevant structure changes

Similar to the estimation of the loci of contact PTs, we estimate the loci of bond PTs. For comparison, we plot these two results together in Fig. 2(a). Quite different from the loci of contact PTs with different interaction ranges, which are



FIG. 6. (a) The normalized distribution of contact cluster size, $n_0(s)$, of systems at different packing fractions, ϕ , with $B_2^* = 0.7$. (b) $n_0(s)$ of systems along contact percolation boundary. Solid lines represent fitting curves for the power law decay of $n_0(s)$ upon percolation. All the results are obtained for $\lambda = 1.05$. See the legend for the meaning of the symbols.

dispersed, the loci of bond PTs with different λ ($\lambda = 1.01, \lambda = 1.05$) merge with the percolation boundary of Baxter sticky model possibly due to the obeying of the extended law of corresponding state. The trade-off between interaction range and statistical weight for bond probability may account for the collapse of bond percolation boundaries, which deserves further investigation.

Different from the critical probability for contact percolation $\Omega_c \sim 0.37$ for different B_2^* , the critical probability for bond percolation Ω_c^* increases when B_2^* increases. For $\lambda = 1.01$, $\Omega_c^* = 0.42$ at $B_2^* = 0.7$, and $\Omega_c^* = 0.37$ at $B_2^* = -0.7$. For $\lambda = 1.05$, $\Omega_c^* = 0.52$ at $B_2^* = 0.7$, and $\Omega_c^* = 0.40$ at $B_2^* = -0.7$. The correlation length exponent for bond percolation ν^* is still invariant to the change of B_2^* . For $\lambda = 1.01$, $\nu^* = 0.97$, while for $\lambda = 1.05$, $\nu^* = 0.96$.

To study the structure changes near the bond percolation boundary, we investigate the behavior of average bond coordination number $\langle z^* \rangle$ defined in Sec. II C. As can be seen from Fig. 7, the value of $\langle z^* \rangle$ is inversely correlated to B_2^* at the same ϕ . Different from the average contact coordination number $\langle z \rangle$, the magnitude of which is very sensitive to the well-width (Fig. 2(b)), the magnitude of $\langle z^* \rangle$ is almost independent of λ at each thermodynamic state points. As B_2^* increases, $\langle z^* \rangle$ as a function of ϕ changes from convex to concave. An approximately linear relationship of $\phi - \langle z^* \rangle$ is obtained around B_2^* = -0.2, which is the same value as the crossing between the contact percolation boundary and the $\langle z \rangle = 2$ isoline shown in Fig. 2(b).

We also plot $\langle z^* \rangle = 2$ isolines on phase diagram Fig. 2(b). As expected, we obtain overlapping isolines for systems with $\lambda = 1.01$ and $\lambda = 1.05$. Since at the same thermodynamic condition $\langle z^* \rangle < \langle z \rangle$, $\langle z^* \rangle = 2$ isolines locate at higher packing fraction, compared with $\langle z \rangle = 2$ isolines at the same B_2^* . When B_2^* is negative, the value of the bond probability, *P*, is closer to 100%, thus the $\langle z^* \rangle = 2$ isoline is closer to the corresponding $\langle z \rangle = 2$ isoline at the same B_2^* . With the increase of B_2^* , *P* decreases, so we observe greater distance between $\langle z^* \rangle$ and $\langle z \rangle$ isolines at larger B_2^* . For system with infinitesimal well-width and infinite well-depth, namely, the Baxter sticky model, the $\langle z^* \rangle$ isoline superimposes on the $\langle z \rangle$ isolines and bond percolation boundaries for



FIG. 7. The average bond coordination number, $\langle z^* \rangle$, as a function of the packing fraction, ϕ , for $\lambda = 1.01$ and 1.05 at different B_2^* . See the legend for the meaning of the symbols. Solid and dashed lines are guides to the eyes.



FIG. 8. (a) The average bond aggregation number, $\langle s^* \rangle$, as a function of packing fraction, ϕ , at different B_2^* . (b) The weight average bond aggregation number, $\langle s^* \rangle_w$, as a function of ϕ at different B_2^* . Dotted lines indicate bond PTs at different B_2^* . Error bars provide the standard deviation after averaging at least 10⁵ configurations. All the results are obtained for $\lambda = 1.05$. See the legend for the meaning of the symbols. Solid and dashed lines are guides to the eyes.

systems with any small values of λ superimpose on those for the Baxter sticky model.

Fig. 8(a) and Fig. 8(b) demonstrate the average bond aggregation number, $\langle s^* \rangle_w$, and weight average bond aggregation number, $\langle s^* \rangle_w$, as function of ϕ , respectively. Compared to the corresponding $\langle s \rangle$ and $\langle s \rangle_w$ for contact percolation at the same B_2^* and ϕ shown in Fig. 4, $\langle s^* \rangle$ and $\langle s^* \rangle_w$ of bond clusters are smaller, especially for larger B_2^* . However, at percolation, the values of the critical average bond aggregation number, $\langle s^* \rangle_w^c$, and the critical weight average bond aggregation number, $\langle s^* \rangle_w^c$, for bond percolation (Fig. 8, dashed lines) are very



FIG. 9. The average bond aggregation number, $\langle s^* \rangle$, as a function of packing fraction, ϕ , for $\lambda = 1.01$ and 1.05 at different B_2^* . Error bars provide the standard deviation after averaging at least 10⁵ configurations. See the legend for the meaning of the symbols. Solid and dashed lines are guides to the eyes.

close to the corresponding values of $\langle s \rangle^c$ and $\langle s \rangle^c_w$ for contact percolation, i.e., $\langle s^* \rangle^c \sim 5$ and $\langle s^* \rangle^c_w \sim 1000$, highlighted by the dashed lines in Fig. 8.

We next investigate the dependence of $\langle s^* \rangle$ on the interaction range, λ . As can be seen from Fig. 9, at $B_2^* = -0.7$, for same ϕ , $\langle s^* \rangle$ for $\lambda = 1.05$ is slightly larger than that for $\lambda = 1.01$. Similar results are obtained at other values of B_2^* . However, such difference in $\langle s^* \rangle$ is very minor, compared to the difference in $\langle s \rangle$ at the same packing fraction in Fig. 5. In addition, we do not observe any increase of the discrepancy in $\langle s^* \rangle$ for $\lambda = 1.05$ and 1.01 with the increase of B_2^* . The results indicate the convergence of the structural properties for systems with different interaction ranges after employing the bond probability into our calculation.

IV. CONCLUSION

To summarize, we investigate the effect of the interaction potentials (with different interaction ranges of SRSW) on the percolation boundaries. We find that the probabilities of contact percolation and bond percolation both obey the scaling behavior. The loci of the contact PTs are strongly dependent on the interaction ranges of SRSW, especially away from the LLCP. However, varying the interaction ranges of SRSW does not affect much the structure along percolation boundaries especially for low packing fractions. For instance, along the percolation boundary, distributions of coordination number show convergence, and distributions of cluster size are universal for different potential interaction ranges considered. In addition, either the bond percolation boundaries or the isolines for average bond coordination number with different interaction ranges collapse to those for Baxter sticky model on phase diagram, which confirms the extended law of corresponding states.

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- ¹D. Stauffer, Phys. Rep. **54**, 1 (1979).
- ²Y. C. Chiew and E. D. Glandt, J. Phys. A: Math. Gen. 16, 2599 (1983).
- ³S. Safran, I. Webman, and G. Grest, Phys. Rev. A **32**, 506 (1985).
- ⁴D. M. Heyes, Mol. Phys. **69**, 559 (1990).
- ⁵D. Stauffer and A. Aharony, *Introduction to Percolation Theory*, 2nd ed. (Taylor & Francis, New York, 2003).

- ⁶M. Miller and D. Frenkel, Phys. Rev. Lett. 90, 135702 (2003).
- ⁷M. A. Miller and D. Frenkel, J. Chem. Phys. **121**, 535 (2004).
- ⁸J. Skvor, I. Nezbeda, I. Brovchenko, and A. Oleinikova, Phys. Rev. Lett. 99, 127801 (2007).
- ⁹L. A. Pugnaloni, C. M. Carlevaro, M. G. Valluzzi, and F. Vericat, J. Chem. Phys. **129**, 064510 (2008).
- ¹⁰J. Skvor and I. Nezbeda, Phys. Rev. E **79**, 041141 (2009).
- ¹¹J. Skvor and I. Nezbeda, Mol. Phys. 109, 133 (2011).
- ¹²H. Neitsch and S. H. L. Klapp, J. Chem. Phys. **138**, 064904 (2013).
- ¹³K. Kroy, M. Cates, and W. Poon, Phys. Rev. Lett. 92, 148302 (2004).
- ¹⁴A. Coniglio, L. D. Arcangelis, E. D. Gado, A. Fierro, and N. Sator, J. Phys.: Condens. Matter 16, S4831 (2004).
- ¹⁵M. A. Miller and D. Frenkel, J. Phys.: Condens. Matter 16, S4901 (2004).
- ¹⁶G. Foffi, C. De Michele, F. Sciortino, and P. Tartaglia, J. Chem. Phys. **122**, 224903 (2005).
- ¹⁷E. Zaccarelli, J. Phys.: Condens. Matter **19**, 323101 (2007).
- ¹⁸J. C. F. Toledano, F. Sciortino, and E. Zaccarelli, Soft Matter 5, 2390 (2009).
- ¹⁹J. M. Tavares, P. I. C. Teixeira, M. M. Telo da Gama, and F. Sciortino, J. Chem. Phys. **132**, 234502 (2010).
- ²⁰S. Babu, J. C. Gimel, and T. Nicolai, J. Chem. Phys. **125**, 184512 (2006).
- ²¹B. Nigro, C. Grimaldi, M. A. Miller, P. Ryser, and T. Schilling, J. Chem. Phys. **136**, 164903 (2012).
- ²²B. Nigro, C. Grimaldi, P. Ryser, F. Varrato, G. Foffi, and P. J. Lu, Phys. Rev. E 87, 062312 (2013).
- ²³E. Dickinson, J. Colloid Interface Sci. 356, 196 (2011).
- ²⁴E. Dickinson, Adv. Colloid Interface Sci. 199-200, 114 (2013).
- ²⁵A. P. R. Eberle, N. J. Wagner, and R. Castaneda-Priego, Phys. Rev. Lett. **106**, 105704 (2011).
- ²⁶A. P. R. Eberle, R. Castaneda-Priego, J. M. Kim, and N. J. Wagner, Langmuir 28, 1866 (2012).
- ²⁷N. Valadez-Perez, Y. Liu, A. Eberle, N. Wagner, and R. Castaneda-Priego, Phys. Rev. E 88, 060302 (2013).
- ²⁸P. J. Lu, E. Zaccarelli, F. Ciulla, A. B. Schofield, F. Sciortino, and D. A. Weitz, Nature **453**, 499 (2008).
- ²⁹D. L. Pagan and J. D. Gunton, J. Chem. Phys. **122**, 184515 (2005).
- ³⁰H. Liu, S. Garde, and S. Kumar, J. Chem. Phys. **123**, 174505 (2005).
- ³¹Y. Duda, J. Chem. Phys. **130**, 116101 (2009).
- ³²N. E. Valadez-Perez, A. L. Benavides, E. Scholl-Paschinger, and R. Castanneda-Priego, J. Chem. Phys. **137**, 084905 (2012).
- ³³D. Costa, P. Ballone, and C. Caccamo, J. Chem. Phys. **116**, 3327 (2002).
- ³⁴E. Zaccarelli, S. V. Buldyrev, E. La Nave, A. J. Moreno, I. Saika-Voivod, F. Sciortino, and P. Tartaglia, Phys. Rev. Lett. **94** (2005).
- ³⁵L. Xu, S. V. Buldyrev, H. E. Stanley, and G. Franzese, Phys. Rev. Lett. 109, 095702 (2012).
- ³⁶S. K. Nayak, P. Jena, K. D. Ball, and R. S. Berry, J. Chem. Phys. **108**, 234 (1998).
- ³⁷S. Babu, J. C. Gimel, and T. Nicolai, J. Chem. Phys. **127**, 054503 (2007).
- ³⁸S. Babu, J. C. Gimel, and T. Nicolai, Eur. Phys. J. E 27, 297 (2008).
- ³⁹J.-C. Gimel and T. Nicolai, J. Phys.: Condens. Matter 23, 234115 (2011).
- ⁴⁰M. N. Bannerman, R. Sargant, and L. Lue, J. Comput. Chem. **32**, 3329 (2011).
- ⁴¹M. G. Noro and D. Frenkel, J. Chem. Phys. **113**, 2941 (2000).
- ⁴²J. Largo, M. A. Miller, and F. Sciortino, J. Chem. Phys. **128**, 134513 (2008).
- ⁴³R. J. Baxter, J. Chem. Phys. **49**, 2770 (1968).
- ⁴⁴N. Sator, Phys. Rep. **376**, 1 (2003).
- ⁴⁵A. Coniglio, J. Phys.: Condens. Matter **13**, 9039 (2001).
- ⁴⁶J.-C. Gimel, T. Nicolai, and D. Durand, Phys. Rev. E 66, 061405 (2002).
- ⁴⁷H. He and M. Thorpe, Phys. Rev. Lett. **54**, 2107 (1985).
- ⁴⁸See supplementary material at http://dx.doi.org/10.1063/1.4906084 for more information on distributions of cluster size.