Extended law of corresponding states for percolation threshold of short-range attractive spheres

JiaChen Wei^{1,2}, and Fan Song^{1,2*}

¹*Institute of Mechanics, Chinese Academy of Sciences, Beijing 100190, China;*

²*School of Engineering Science, University of Chinese Academy of Sciences, Beijing 100049, China*

Received September 3, 2016; accepted October 21, 2016; published online November 2, 2016

Citation: J. C. Wei, and F. Song, Extended law of corresponding states for percolation threshold of short-range attractive spheres. *Sci. China-Phys. Mech. Astron.* **60**, 014621 (2017), doi: 10.1007/s11433-016-0355-2

The percolation threshold (PT) for colloidal system refers to the point at which particles aggregate to form an infinite cluster that spans the suspension [1]. It is widely assumed that the percolation transition should follow the concept of scaling, and recent numerical studies [2-5] have shown that the wrapping probability of percolation can be described by the universal scaling functions, which enables the estimation of PTs for different types of system.

Interestingly, the loci of the PTs for the colloidal system on a phase diagram depend on the specific definition of the cluster [6]. By choosing a cutoff distance d (e. g. $d = \sigma + \lambda$ for the system of square-well interactions, where σ is the particle diameter and λ the well width), the contact cluster is defined as an ensemble of particles with interparticle distance smaller than d . An alternative way to define a cluster is energy-based [2, 6]. For each configuration, we construct fictitious bonds between particles i and j with bond probability

$$P(r_{ij}) = 1 - e^{c\beta U_{ij}(r_{ij})}, \quad (1)$$

where $U_{ij}(r_{ij})$ is interactive potential, c is the weighting factor, and $\beta = 1/kT$ (with k the Boltzmann factor and T the temperature). The bond cluster (with $c = 1$) and Conglio-Klein (CK) cluster (with $c = 1/2$) are then defined as an ensemble of particles that are linked by bonds. A third type of cluster—Hill cluster [4]—takes into account the proximity of the particles in the phase space. For Hill cluster, particle i and j are linked if their relative kinetic energy is lower than their

attractive energy, which can be written as:

$$\frac{m}{4} (\mathbf{v}_i - \mathbf{v}_j)^2 \leq -U_{ij}, \quad (2)$$

where $\mathbf{v}_i$ and $\mathbf{v}_j$ are their velocity vectors, and m is the mass.

We have shown in our recent work [2] that, for contact clusters, PTs are strongly dependent on the interaction ranges, which is clearly inconsistent with the Noro-Frenkel extended law of corresponding states [2, 7]. According to the law, the loci of phase boundaries for all types of short-range attractive systems can be mapped to that for Baxter sticky model [7] on $B_2^* - \phi$ phase diagram, where B_2^* and ϕ respectively denote the reduced second virial coefficient and the packing fraction of the system. Therefore, we anticipate such law of scaling would also apply to percolation boundaries if an appropriate and physically-reasonable definition of cluster is chosen. In this letter, we will compare PTs for different definitions of cluster, and investigate which types of PTs are more converged on phase diagram, i.e., consistent with the extended law of corresponding states.

We simulate monodisperse hard-spheres interacting with short-range square-well (SRSW) potential [7-9] contained in a cubic box with periodic boundary condition. Event-driven molecular dynamics simulations [10] are implemented in NVT-ensemble. A cluster percolates the system when any particle within the cluster can be connected to its image in another replica (see previous papers [2, 4] for details). The contact, CK, bond, and Hill PTs are determined respectively once the corresponding contact, CK, bond, or Hill cluster wraps the system.

*Corresponding author (email: songf@lm.imech.ac.cn)

Figure 1 provides the loci of PTs of different types obtained by simulation. The contact and CK percolation boundaries for different values of λ show dispersion (Figure 1(a)). For instance, the percolation boundaries for contact clusters are very dispersed when $B_2^* > 0.0$. At fixed B_2^* , as λ decreases from 1.05 to 1.01, PT becomes larger for contact and smaller for CK case. Nevertheless, if λ is further decreased to infinitesimally small, both contact and CK PTs of SRSW system reduce to that for Baxter sticky model, as shown in Figure 1(a) by the dashed blue line. In our calculation, the critical probability for both contact and CK percolation is independent of the value of B_2^* and λ . The correlation length exponent for contact and CK percolation is also independent of the value of B_2^* , but slightly dependent on λ .

For comparison, the loci of bond and Hill PTs are plotted together in Figure 1(b). Quite different from the case of contact PTs, which are dispersed, the loci of bond and Hill PTs with different λ ($\lambda = 1.01$ and $\lambda = 1.05$) collapse onto the percolation boundary for Baxter sticky model, which confirms with the extended law of corresponding state. Note that such scaling behavior is observed for all thermodynamic states taken into account, with the value of B_2^* varying from -0.7 to 0.9 . The critical probability for bond and Hill percolation increases when B_2^* increases, while the correlation length exponent is still invariant to the change of B_2^* .

Figure 1 (Color online) Phase diagram for SRSW system with (a) contact (black) and CK (magenta) PTs, and (b) bond (blue) and Hill (red) PTs, of different λ . While green stars are mapped liquid-liquid phase separation (LLPS) and critical points [5] for $\lambda = 1.01$, navy stars represent that for $\lambda = 1.05$. Blue dashed line is the percolation boundary for Baxter sticky model [7]. The other lines are to guide the eye, and error bars are smaller than symbol sizes.

While bond percolation boundaries ($c = 1$) collapse to that for Baxter sticky model on phase diagram, the CK percolation boundaries ($c = 1/2$) with different interaction ranges show dispersion. This indicates the scaling behavior of PTs is very sensitive to the value of c . Interestingly, by analyzing the loci of PTs for other values of c (e. g. $c = 1.5$ and $c = 0.7$), we find the scaling only takes place when $c = 1$. One possible explanation is that the effective probability of bonding for the real bond-on/off system [11] equals $1 - \exp(-U/kT)$, which is exactly the same as the formation probability of the fictitious bonds for bond percolation.

Note that the percolation boundaries for lattice gas model with varied c were previously investigated [6, 12]. It was estimated that the Hill percolation boundary, which starts at the critical point, should be very close to the CK percolation boundary (with $c = 1/2$) for the lattice gas model. However, our 3D off-lattice simulations clearly demonstrate that the loci of Hill PTs are quite close to bond PTs, both of which show scaling and collapse to that for Baxter sticky model. In addition, the bond percolation boundaries start from the left branch of LLPS line in the low-density region rather than the critical point for our off-lattice system. This leads us to anticipate the existence of the mesophase above the LLPS line, which was first proposed by Heyes et al. [13]. According to their analysis, the mesophase is bounded by the percolation boundaries of clusters and available volumes of the system, and the critical point is replaced with the critical dividing line.

The author thanks help from Dr. Marcus Bannerman. This work was supported by the National Natural Science Foundation of China (Grant Nos. 11602279, 11232013, and 11472285).

- 1 D. Stauffer, and A. Aharony, *Introduction to Percolation Theory* (Taylor & Francis, New York, 2003).
- 2 J. Wei, L. Xu, and F. Song, *J. Chem. Phys.* **142**, 034504 (2015).
- 3 J. Skvor, I. Nezbeda, I. Brovchenko, and A. Oleinikova, *Phys. Rev. Lett.* **99**, 127801 (2007).
- 4 J. Skvor, and I. Nezbeda, *Phys. Rev. E* **79**, 041141 (2009).
- 5 H. Neitsch, and S. H. L. Klapp, *J. Chem. Phys.* **138**, 064904 (2013).
- 6 N. Sator, *Phys. Rep.* **376**, 1 (2003).
- 7 M. G. Noro, and D. Frenkel, *J. Chem. Phys.* **113**, 2941 (2000).
- 8 L. Xu, S. V. Buldyrev, H. E. Stanley, and G. Franzese, *Phys. Rev. Lett.* **109**, 095702 (2012).
- 9 Y. Duda, *J. Chem. Phys.* **130**, 116101 (2009).
- 10 M. N. Bannerman, R. Sargant, and L. Lue, *J. Comput. Chem.* **32**, 3329 (2011).
- 11 S. Babu, J. C. Gimel, and T. Nicolai, *J. Chem. Phys.* **125**, 184512 (2006).
- 12 A. Coniglio, *J. Phys. Condens. Matter* **13**, 9039 (2001).
- 13 D. M. Heyes, and L. V. Woodcock, *Fluid Phase Equilib.* **356**, 301 (2013).