

## ARTICLE

# Effect of Impurity on Critical Conditions of Colloidal Cluster Nucleation in Colloidal System

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Due to depletion interactions, a few of colloidal spheres will be packed into cluster or clusters, even a phase transition may take place if the volume fraction of system is large enough. In a binary colloidal system, if the mole fraction of one component is very small, then it can be taken as the impurity of the other component. In this work, the effect of impurity on critical conditions of colloidal cluster nucleation was studied by Carnahan-Starling state equation and the principle of entropy maximum. The results show that, even the mole fraction of small-spheres is very small, the critical volume fraction is obvious smaller than that of one component system, so the influence on critical volume fraction from impurity is very huge and cannot be ignored. In addition, it is also found that, the larger the volume fraction of the system is, the larger cluster density can be packed, however, the critical size of nucleating cluster is almost independent of the density of the cluster.

**Key words:** Cluster sphere, Cluster density, Cluster nucleation

## I. INTRODUCTION

Colloidal solutions are always interesting topics for both the chemists and physicists, and much attention has been paid to colloidal particles, largely due to their mechanisms of ordering and self-assembly, cooperative motion, phase transition, and their application in optics as photonic materials. As is known that equations of state have been actively studied [1–6], leading to several methods to predict the osmotic pressure and stability of colloidal particles [7, 8]. Hydrodynamic theories combined with the equation of state as well as the mode-coupling theory have also been applied to investigate the diffusion properties of colloidal particles dispersed in solutions [9, 10]. Du *et al.* have studied the influence of sedimentation on crystallization of charged colloidal particles [11]. Recently, the cluster formation of colloidal particles attracts increasing attention [12, 13]. In this work, by combining the state equation and maximum entropy principle, we study the influence of impurity on cluster nucleation forming.

It is well known that there are depletion interactions among colloidal spheres [14, 15], a few of colloidal spheres will be packed into cluster or clusters, even a phase transition may take place if the volume fraction of the system is large enough [12, 16, 17]. Usually the phase transition in complex fluids is studied through

the density functional theory [18, 19]. However, in hard-sphere system, the phase transition caused by depletion interactions is entropy-driven, and there are two competing effects on entropy at the same time when spheres are packed: one is the entropy increase caused by the increase of free volume, the other is the entropy decrease caused by the decrease of unpacked spheres, so the critical condition can be obtained directly by analyzing the variation of entropy through the state equation of the system [20, 21].

Recently, the cluster is even taken as a new kind of sphere of the system, so the binary system turns to be a ternary one consisting of small and large spheres and cluster sphere. In fact, the “cluster sphere” is very helpful for determining the critical condition [12]. The most distinguished character of cluster sphere is that its size is not constant, and the packing model related to the arrangement of spheres in space is various. When the size of cluster sphere is large enough, it is nucleated and a new phase will turn out, so the critical condition of cluster nucleation is almost the condition denoting phase transition. Furthermore, a special case of the binary system may relate to a new subject: if the mole fraction of one component is very small, it can be taken as impurity of the other component. Obviously, it is easy to analyze quantitatively the influence of impurity on critical condition of phase transition in this way. In this work, the ternary Carnahan-Starling (CS) state equation [1] is used to study the influence of impurity on critical condition of nucleation, including the critical size of nucleating cluster and the corresponding volume fraction of system, through changing the mole fraction

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of one component to minuteness.

## II. MODEL AND THEORETICAL ANALYSIS

In general, the entropy of system consisting of  $m$  kinds of hard spheres can be written as [1],

$$S = Nk_B \left[ \frac{3}{2}(1 - y_1 + y_2 + y_3) - \frac{3y_2 + 2y_3}{1 - \xi} - \frac{3}{2} \left( 1 - y_1 - y_2 - \frac{1}{3}y_3 \right) \frac{1}{(1 - \xi)^2} - (y_3 - 1) \ln(1 - \xi) + \ln Z \right] \quad (1)$$

where

$$Z = [(1 + \xi + \xi^2) - 3\xi(y_1 + y_2\xi) - \xi^3y_3] \frac{1}{(1 - \xi)^3} \quad (2)$$

$$\xi = \sum_{i=1}^m \xi_i, \quad \xi_i = \frac{1}{6} \pi \rho d_i^3 x_i, \quad \sum_{i=1}^m x_i = 1, \quad x_i = \frac{N_i}{N} \quad (3)$$

$$y_1 = \sum_{j>i=1}^m \Delta_{ij} \frac{d_i + d_j}{(d_i d_j)^{1/2}} \quad (4)$$

$$y_2 = \sum_{j>i=1}^m \Delta_{ij} \sum_{k=1}^m \frac{\xi_k (d_i d_j)^{1/2}}{\xi d_k} \quad (5)$$

$$y_3 = \left[ \sum_{i=1}^m \left( \frac{\xi_i}{\xi} \right)^{2/3} x_i^{1/3} \right]^3 \quad (6)$$

in which  $\rho$  stands for the number density of colloidal particles,  $N_i$ ,  $d_i$ , and  $x_i$  are the number, diameter, and mole fraction of the  $i$ -th component, respectively, and

$$\Delta_{ij} = \frac{(\xi_i \xi_j)^{1/2} (d_i - d_j)^2}{\xi d_i d_j} (x_i x_j)^{1/2} \quad (7)$$

Though some modifications has been made on the CS equation in recent years [3–5], we still use CS equation for the system in which the density is not very high, just because of its the simplicity and accurateness.

In this work, we only take the case  $m=3$  into consideration: the three components are the small-sphere and large-sphere and cluster. Firstly, it is useful to introduce the concept of cluster sphere corresponding to the  $k$ -cluster. Let  $d_3(k)$  denotes the diameter of the cluster sphere. It is reasonable to suppose that the volume of  $k$ -cluster and the corresponding cluster sphere are the same, then  $d_3(k)$  can be determined through the relation,

$$k \frac{4}{3} \pi \left( \frac{d_2}{2} \right)^3 = \frac{4}{3} \pi \left( \frac{d_3}{2} \right)^3 \phi \quad (8)$$

and is written as

$$d_3 = d_2 \left( \frac{k}{\phi} \right)^{1/3} \quad (9)$$

where  $\phi$  is the density or packing fraction of the  $k$ -cluster or cluster sphere. Obviously, the value of  $\phi$  is related to the space structure of the packing spheres, for example, if the cluster is packed into the face-centered cubic (fcc), then  $\phi=0.74$ ; for the body-centered cubic (bcc) structure,  $\phi=0.64$ ; for the glass state,  $\phi=0.58$ .

When the size of a cluster sphere is larger than the critical size, it is nucleating or nucleated and a new phase will turn out. According to the principle of maximum entropy, the critical size of cluster and the corresponding volume fraction of the system can be determined as follows:

$$\frac{dS}{dN_2} = 0 \quad (10)$$

Obviously,  $S$  is the function of  $N_2$  and  $d_3(k)$ , where  $k$  is related to  $N_2$ , so the above formula can be further written as,

$$\frac{\partial S}{\partial N_2} + \frac{\partial S}{\partial d_3} \frac{\partial d_3}{\partial N_2} = 0 \quad (11)$$

where

$$\begin{aligned} \frac{\partial S}{\partial N_2} = & \frac{S}{N} + Nk_B \left\{ \frac{3}{2} \left( -\frac{\partial y_1}{\partial N_2} + \frac{\partial y_2}{\partial N_2} + \frac{\partial y_3}{\partial N_2} \right) - \left( 3 \frac{\partial y_2}{\partial N_2} + 2 \frac{\partial y_3}{\partial N_2} \right) \frac{1}{1 - \xi} - \frac{3y_2 + 2y_3}{(1 - \xi)^2} \frac{\partial \xi}{\partial N_2} + \frac{3}{2} \left( \frac{\partial y_1}{\partial N_2} + \frac{\partial y_2}{\partial N_2} + \frac{1}{3} \frac{\partial y_3}{\partial N_2} \right) \frac{1}{(1 - \xi)^2} - 3 \left( 1 - y_1 - y_2 - \frac{1}{3}y_3 \right) \frac{1}{(1 - \xi)^3} \frac{\partial \xi}{\partial N_2} - \frac{\partial y_3}{\partial N_2} \ln(1 - \xi) + \frac{y_3 - 1}{1 - \xi} \frac{\partial \xi}{\partial N_2} + \frac{1}{Z} \frac{\partial Z}{\partial N_2} \right\} \quad (12) \end{aligned}$$

$$\begin{aligned} \frac{\partial S}{\partial d_3} = & Nk_B \left\{ \frac{3}{2} \left( -\frac{\partial y_1}{\partial d_3} + \frac{\partial y_2}{\partial d_3} + \frac{\partial y_3}{\partial d_3} \right) - \left( 3 \frac{\partial y_2}{\partial d_3} + 2 \frac{\partial y_3}{\partial d_3} \right) \frac{1}{1 - \xi} - \frac{3y_2 + 2y_3}{(1 - \xi)^2} \frac{\partial \xi}{\partial d_3} + \frac{3}{2} \left( \frac{\partial y_1}{\partial d_3} + \frac{\partial y_2}{\partial d_3} + \frac{1}{3} \frac{\partial y_3}{\partial d_3} \right) \frac{1}{(1 - \xi)^2} - 3 \left( 1 - y_1 - y_2 - \frac{1}{3}y_3 \right) \frac{1}{(1 - \xi)^3} \frac{\partial \xi}{\partial d_3} - \frac{\partial y_3}{\partial d_3} \ln(1 - \xi) + \frac{y_3 - 1}{1 - \xi} \frac{\partial \xi}{\partial d_3} + \frac{1}{Z} \frac{\partial Z}{\partial d_3} \right\} \quad (13) \end{aligned}$$

$$\frac{\partial d_3}{\partial N_2} = -\frac{1}{3\phi} \frac{d_2^3}{d_3^2} \quad (14)$$

All the concrete partial derivatives related to Eqs. (12) and (13) are listed in Supplementary material. If all the related expressions are put into Eq.(10) or Eq.(11), it will become very complex. However, the idea and strategy of our theory are very simple and concise: there are only four parameters  $\xi$ ,  $k$ ,  $x_i$ ,  $\phi$  related to Eq.(10) or Eq.(11), and two of them  $k$ ,  $\phi$  are related to the cluster,

TABLE I Critical cluster size and corresponding volume fraction in case of  $x_2=0.99, 0.999, 0.9999$ , and  $\phi=0.74, 0.64, 0.58$ .

$x_2$	$\phi$	$\xi$	$k$	$\xi_2$	$\xi_1$
0.99	0.74	0.46–0.52	24–30	0.4595905–0.5195371	0.0004095–0.0004629
	0.64	0.45–0.50	22–29	0.4495994–0.4995549	0.0004006–0.0004451
	0.58	0.44–0.49	22–27	0.4396083–0.4895638	0.0003917–0.0004362
0.999	0.74	0.47–0.53	23–29	0.4695816–0.5295281	0.0004184–0.0004719
	0.64	0.45–0.51	22–27	0.4495994–0.5095460	0.0004006–0.0004540
	0.58	0.44–0.50	21–26	0.4396083–0.4995549	0.0003917–0.0004451
0.9999	0.74	0.48–0.54	21–26	0.4799958–0.5399952	0.0000042–0.0000048
	0.64	0.46–0.52	21–26	0.4599959–0.5199954	0.0000041–0.0000046
	0.58	0.45–0.50	21–26	0.4499960–0.4999956	0.0000040–0.0000044

and the value of  $\phi$  will be given in previous. So it is easy to determine the relation between  $k$  and  $\xi$  for a given  $\phi$ . Yet, it is useful to emphasize that the principle in above discussions is only applicable to the hard sphere system, not to the systems with attractive or repulsive interactions among the components, including the systems with the van der Waals attractive forces, because the energy of these systems will change when the cluster is formed.

### III. RESULTS AND DISCUSSION

To investigate the influence of the impurity, the system under consideration should be that the mole fraction of large-spheres is far larger than that of the small ones. So the character of the system is mainly determined by the large spheres, and the small spheres are taken as impurity. In our systems, the diameters of the small-sphere and large-sphere are  $d_1=6.9\times 10^{-8}$  m and  $d_2=1.55\times 10^{-7}$  m respectively, and three mole fractions of large sphere with  $x_2=0.99, 0.999, 0.9999$  in the cases of  $\phi=0.74, 0.64, 0.58$  are studied by Eq.(10) or Eq.(11), and the results of the critical cluster size and the corresponding volume fraction are determined and listed in Table I respectively.

From Table I, it is easy to get the following three points about the influence of impurity on critical condition: (i) for the case of  $\phi=0.74$ , when  $x_2=0.99, 0.999$ , and  $0.9999$ , the corresponding volume fractions are  $\xi=0.46, 0.47$ , and  $0.48$ , respectively. Obviously, the critical volume fraction  $\xi$  increases from  $0.46$  to  $0.48$  when the mole fraction of large-sphere  $x_2$  increased from  $0.99$  to  $0.9999$ . In fact, the critical volume fraction of one component system is  $\xi=0.495$ , so even the mole fraction of impurity is  $x_1=0.00001$ , the critical volume fraction decreases from  $0.495$  to  $0.48$ , and the influence of impurity on the nucleation condition is obviously huge, and it is reasonable to believe that  $\xi$  will tend to  $0.495$  when  $x_1\rightarrow 0$  [16]. The same conclusion can also be obtained for the cases of  $\phi=0.64, 0.58$ . (ii) On the other hand, for a given volume fraction, there is a specific number  $k$  denoting the critical cluster size. From Table I,

we also found that, for fcc, when  $x_2=0.99$  and  $\xi=0.46$ , the critical size of nucleating cluster  $k$  is  $30$ , it will change to  $24$  when  $\xi=0.53$ ; corresponding to  $x_2=0.999$  and  $\xi=0.47-0.53$ , we get  $k=29-23$ ; as  $x_2=0.9999$  and  $\xi=0.48-0.54$ ,  $k=29-21$ , *i.e.*, when  $x_2$  changes from  $0.99$  to  $0.9999$ , the corresponding  $\xi=0.47\rightarrow 0.49$ , and  $k=30\rightarrow 29$ , so the critical size is almost independent of the mole fraction of large-spheres. The same conclusion can also be obtained for the other two different structures. (iii) Only the glass state corresponding to  $\phi=0.58$  can be formed when  $\xi=0.45$ , however, one can get the bcc structure corresponding to  $\phi=0.64$  when  $\xi=0.46$ , even the fcc structure corresponding to  $\phi=0.74$  can be obtained when  $\xi=0.48$ , *i.e.*, the larger the volume fraction of the system is, the larger cluster density can be packed.

### IV. CONCLUSION

In conclusion, the influence of impurity on critical conditions of cluster nucleation were studied through the combination of cluster sphere, CS state equation, and the principle of maximum of entropy, and it is found that, as impurity, though the mole fraction of small-sphere is very small, the critical volume fraction of system for cluster to nucleate is strongly affected; on the other hand, the critical size of nucleating cluster is almost unaffected by the impurity. In addition, we also found that the density of the nucleating cluster increases with the increase of volume fraction.

**Supplementary material:** All the concrete partial derivatives related to Eqs. (12) and (13) are listed.

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