Critical volume fraction and size for a colloidal cluster to nucleate*

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With the aid of the critical size of colloidal cluster, the critical volume fraction of phase transition of colloidal system is determined by the principle of entropy maximum and Carnahan–Starling (CS) state equation in this paper. In our discussion, no parameter is introduced externally, and our results are in good agreement with the experimental results.

Keywords: depletion interaction, nucleation packing, cluster

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The phase behaviour of a colloidal system is very complex, and it has attracted considerable attention in recent years.[1−15] Experimentally, it has been observed that with the increase of sphere concentration, there appears an evolution from colloidal fluid to a phase of fluid-crystal coexistence, and finally to a fully crystalline phase. It is also predicted by the computer simulations with Monte Carlo and molecular dynamics methods. In the view of theoretical analyses, that can be easily obtained from a qualitative discussion. It is known that in a colloidal system consisting of spheres, there are excluded volumes around them.[1,2] When the spheres approach each other so closely that their excluded volumes overlap, the spheres are packed together, forming a "cluster" consisting of the packed spheres. In this process, not only the free volume for other isolated spheres but also the entropy of the system are increased. According to the principle of entropy maximum, the large spheres will be further packed. If the spheres are packed into many clusters at the same time, the packing takes place among these clusters rather than other spheres. As a result, the cluster grows larger and larger and turns into a nucleation, and brings on a new phase of fluid-crystal coexistence. However, in this packing process, there is a competing factor resulting in entropy decreasing: when a part of spheres pack together, the number of isolated spheres decreases, resulting in a decrease of entropy. So, there is a critical volume fraction for large spheres to nucleate. However, it is very difficult to achieve a critical volume fraction from a quantitative analysis. Fortunately, some quantitative results were obtained directly through the expression of entropy obtained from the CS state equation,[4−6] but a modified parameter was introduced in the discussion, so further investigations are still needed. In this paper, we first review the quantitative analyses discussed previously, then a modified method will be discussed.

For a binary hard-sphere system confined in a container with a fixed volume V, the entropy is closely related to the numbers of the large and the small spheres ($N_{\rm L}$ and $N_{\rm S}$), the free volume $V_{\rm f}$, and it can be generally written as[5]

$$S = S(N_{\rm L}, N_{\rm S}, V_{\rm f}). \tag{1}$$

Driven by the small spheres, a part of the large spheres are aggregated. In this process, the number $N_{\rm S}$ does not change while the number $N_{\rm L}$ decreases, and the variation of the entropy S can be written as

$$\delta S = \frac{\partial S}{\partial N_{\rm L}}\delta N_{\rm L} + \frac{\partial S}{\partial V_{\rm f}}\frac{\partial V_{\rm f}}{\partial N_{\rm L}}\delta N_{\rm L}. \tag{2}$$

The critical volume fraction is determined through the equation

$$\frac{\partial S}{\partial N_{\rm L}} + \frac{\partial S}{\partial V_{\rm f}}\frac{\partial V_{\rm f}}{\partial N_{\rm L}} = 0$$

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if the analytical expression of the entropy S is obtained. Fortunately, with the aid of CS state equation, the entropy of the hard-sphere system can be analytically expressed. However, when the critical volume fraction is obtained in this way, it is found that the calculated value is smaller than the measured one.[14] In fact, only a part of excluded volumes of two large spheres overlap when they pack together, so a parameter was introduced to modify the volume variation, $\partial V_{\rm f}/\partial N_{\rm L}$, and a better result was obtained in Ref. [5].

Besides the two factors mentioned above, the other factors should be considered in the packing process. For example, when large spheres pack into a cluster through the nucleation packing, its size increases continuously. In fact, only when the size of the cluster is large enough, can it turn into a nucleation, then a phase transition can take place. If the cluster is taken to be a larger sphere, then the binary colloidal system turns into a system consisting of three kinds of spheres: cluster, large sphere, and small sphere. So the entropy described by Eq. (1) will be rewritten as

$$S = S(N_{\rm c}, N_{\rm L}, N_{\rm S}, V_{\rm f}, d_{\rm c}), \tag{3}$$

where $N_{\rm c}$ and $d_{\rm c}$ denote the number and the diameter of the cluster respectively. We note that in the nucleation packing process, the size of the cluster increases continuously, so the diameter becomes a very important parameter which will be discussed in this paper. Obviously equation (3) is more complicated than Eq. (1). To make the problem simplified, in this paper we consider a unit sphere system, the system that consists of the equal-sized hard spheres of the same kind. Suppose that in the nucleation packing process, the number of the cluster keeps constant, so the entropy of this system is closely related to the number of the unpacked spheres, $N_{\rm c}$, the free volume of the spheres $V_{\rm f}$, and the size of the cluster $d_{\rm c}$, and then equation (3) can then be written as

$$S = S(N_{\rm S}, V_{\rm f}, d_{\rm c}). \tag{4}$$

When k spheres pack into a cluster, the system turns into a binary system consisting of $N-k$ hard spheres and a large cluster, and can still be dealt with in the framework of a binary system. In the nucleation packing, the number of the clusters is kept at 1 while the number of the isolated spheres decreases by k, and the critical volume fraction can then be determined by the principle of entropy maximum,

$$\delta S = \frac{\partial S}{\partial N_{\rm S}}\delta N_{\rm S} + \frac{\partial S}{\partial d_{\rm c}}\frac{\partial d_{\rm c}}{\partial N_{\rm S}}\delta N_{\rm S}. \tag{5}$$

Fortunately, for a binary mixture composed of $N_{\rm L} = c_{\rm L}N$ large spheres with diameter $d_{\rm L}$ and $N_{\rm S} = c_{\rm S}N$ small spheres with diameter $d_{\rm S}$ (where $c_{\rm S}$ and $c_{\rm L}$ are densities of spheres satisfying $c_{\rm L}+c_{\rm S}=1$), the entropy S can be analytically obtained through the generalized CS equation:[7,8]

$$S_{\rm hs} = S_{\rm gas} + S_{\rm c} + S_\eta + S_\sigma, \tag{6}$$

where

$$\begin{aligned}
S_{\rm gas} &= Nk_{\rm B}\ln\left[e\Omega\left(em_{\rm L}^{c_{\rm L}}m_{\rm S}^{c_{\rm S}}\frac{2\pi k_{\rm B}T}{h^2}\right)^{3/2}\right],\\
S_{\rm c} &= -Nk_{\rm B}\left(c_{\rm L}\ln c_{\rm L} + c_{\rm S}\ln c_{\rm S}\right),\\
S_\eta &= -Nk_{\rm B}\left(\zeta-1\right)\left(\zeta+3\right),\\
S_\sigma &= Nk_{\rm B}\Big\{\frac{3}{2}\left(\zeta^2-1\right)y_1 + \frac{3}{2}\left(\zeta-1\right)^2 y_2\\
&\quad - \left[\frac{1}{2}\left(\zeta-1\right)\left(\zeta-3\right)+\ln\zeta\right]\left(1-y_3\right)\Big\}.
\end{aligned}$$

Here, ω is the mean volume and d is the mean diameter of a sphere, which are related by the following expression:

$$\omega = \frac{\pi}{6}(c_{\rm L}d_{\rm L}^3 + c_{\rm S}d_{\rm S}^3) = \frac{\pi}{6}d^3;$$

$\Omega = V/N$ is the average volume of a sphere; $m_{\rm L}$ and $m_{\rm S}$ are the masses of a large sphere and a small sphere; the relevant parameters are defined as follows:

$$\begin{aligned}
\zeta &= (1-\eta)^{-1},\\
y_1 &= \frac{c_{\rm L}c_{\rm S}(d_{\rm L}+d_{\rm S})(d_{\rm L}-d_{\rm S})^2}{d^3},\\
y_2 &= \frac{c_{\rm L}c_{\rm S}d_{\rm L}d_{\rm S}(c_{\rm L}d_{\rm L}^2 + c_{\rm S}d_{\rm S}^2)(d_{\rm L}-d_{\rm S})^2}{d^6},
\end{aligned}$$

and

$$y_3 = \frac{(c_{\rm L}d_{\rm L}^2 + c_{\rm S}d_{\rm S}^2)^3}{d^6};$$

the constant $e = 2.71828$; $1-\eta$ is the free volume fraction. Except for the cases of higher densities and/or larger diameter ratios of large sphere to small sphere, the validity of Eq. (6) is verified by numerical results.

If a cluster composed of k spheres can be regarded as a large sphere, then its mass is $m_{\rm L} = km_{\rm S}$. However, the size of the cluster is related to its structure or to its density. Assume that the densities of the hard sphere and the cluster are 1 and ρ respectively, then the diameter of the cluster can be determined to be

$$d_{\rm L}(k) = \left(\frac{k}{\rho}\right)^{1/3} d_{\rm S}, \tag{7}$$

through the relation

$$k\frac{4}{3}\pi\left(\frac{d_{\rm S}}{2}\right)^3 = \frac{4}{3}\pi\left(\frac{d_{\rm L}}{2}\right)^3.$$

According to the principle of entropy maximum, the critical volume fraction and the critical size for the cluster to nucleate can then be obtained through the follow equation:

$$\frac{\mathrm{d}S}{\mathrm{d}N_{\mathrm{S}}} = \frac{\partial S}{\partial N_{\mathrm{S}}} + \frac{\partial S}{\partial d_{\mathrm{L}}}\frac{\partial d_{\mathrm{L}}}{\partial N_{\mathrm{S}}} = 0, \tag{8}$$

where

$$\begin{aligned}\frac{\partial S}{\partial N_{\mathrm{S}}} &= \frac{\partial S_{\mathrm{gas}}}{\partial N_{\mathrm{S}}} + \frac{\partial S_{\mathrm{c}}}{\partial N_{\mathrm{S}}} + \frac{\partial S_{\eta}}{\partial N_{\mathrm{S}}} + \frac{\partial S_{\sigma}}{\partial N_{\mathrm{S}}} \\ &= k_{\mathrm{B}}\left[\ln\frac{V}{N_{\mathrm{S}}+1} + \frac{3}{2}\ln\frac{2\pi e m_{\mathrm{S}} k_{\mathrm{B}} T}{h^2}\right] - k_{\mathrm{B}}\ln c_{\mathrm{S}} - k_{\mathrm{B}}\left(\zeta^2+2\zeta-3\right) - \frac{\pi\left(N_{\mathrm{S}}+1\right)}{3V}k_{\mathrm{B}}d_{\mathrm{S}}^3\left(\zeta^3+\zeta^2\right) \\ &\quad + k_{\mathrm{B}}\left\{\frac{3}{2}\left(\zeta^2-1\right)y_1 + \frac{3}{2}\left(\zeta-1\right)^2 y_2 - \left[\frac{1}{2}\left(\zeta-1\right)\left(\zeta-3\right)+\ln\zeta\right]\left(y_1+y_2\right)\right\} + \left(N_{\mathrm{S}}+1\right)k_{\mathrm{B}} \\ &\quad \times\left\{\frac{\pi}{6V}d_{\mathrm{S}}^3\left(2\zeta^3+2\zeta^2-\zeta\right)y_1 + \frac{\pi}{6V}d_{\mathrm{S}}^3\left(2\zeta^3-\zeta^2-\zeta\right)y_2\right. \\ &\quad \left. + \left(\zeta^2+2\zeta-\ln\zeta-3\right)\frac{\partial y_1}{\partial N_{\mathrm{S}}} + \left(\zeta^2-\zeta-\ln\zeta\right)\frac{\partial y_2}{\partial N_{\mathrm{S}}}\right\}. \end{aligned} \tag{9}$$

Assuming that the number of the small spheres is so large that $N \to \infty$, then $N_{\mathrm{S}} \to \infty$, $c_{\mathrm{L}} \to 0$, and $c_{\mathrm{S}} \to 1$, so

$$\frac{\partial S}{\partial N_{\mathrm{S}}} = k_{\mathrm{B}}\left[\ln\frac{V}{N_{\mathrm{S}}+1} + \frac{3}{2}\ln\frac{2\pi e m_{\mathrm{S}} k_{\mathrm{B}} T}{h^2}\right] - k_{\mathrm{B}}\left(\zeta^2+2\zeta-3\right) - \frac{\pi\left(N_{\mathrm{S}}+1\right)}{3V}k_{\mathrm{B}}d_{\mathrm{S}}^3\left(\zeta^3+\zeta^2\right). \tag{10}$$

By the same way we also obtain

$$\begin{aligned}\frac{\partial S}{\partial d_{\mathrm{L}}} &= \frac{\partial S_{\mathrm{gas}}}{\partial d_{\mathrm{L}}} + \frac{\partial S_{\mathrm{c}}}{\partial d_{\mathrm{L}}} + \frac{\partial S_{\eta}}{\partial d_{\mathrm{L}}} + \frac{\partial S_{\sigma}}{\partial d_{\mathrm{L}}} \\ &= \frac{9\rho k_{\mathrm{B}}}{2k d_{\mathrm{S}}}\left(\frac{k}{\rho}\right)^{-2/3} - \frac{\pi(N_{\mathrm{S}}+1)k_{\mathrm{B}}}{V}d_{\mathrm{L}}^2(\zeta^3+\zeta^2) + k_{\mathrm{B}}\left[(\zeta^2+2\zeta-\ln\zeta-3)\frac{\partial y_1}{\partial d_{\mathrm{L}}} + (\zeta^2-\zeta-\ln\zeta)\frac{\partial y_2}{\partial d_{\mathrm{L}}}\right]. \end{aligned} \tag{11}$$

And

$$\frac{\partial y_1}{\partial d_{\mathrm{L}}} = 0, \tag{12a}$$

$$\frac{\partial y_2}{\partial d_{\mathrm{L}}} = 0, \tag{12b}$$

$$\frac{\partial d_{\mathrm{L}}}{\partial N_{\mathrm{S}}} = -\frac{d_{\mathrm{S}}}{3\rho}\left(\frac{k}{\rho}\right)^{-2/3}. \tag{12c}$$

Now we see that the relation between the volume fraction η and the critical size of cluster k is described through Eq. (8). Just like Refs. [4]–[6], in this paper we also suppose that the diameter and the mass of a small sphere are $d_{\mathrm{S}} = 6.9 \times 10^{-8}$ m, and $m_{\mathrm{S}} = 3.2 \times 10^{-24}$ kg respectively, and the temperature $T = 300$ K. Then the relation between η and k can be numerically determined through Eq. (8).

First, we study the case of $\rho = 0.74$, which is corresponding to fcc structure. The numerical results are obtained by solving Eq. (8). From the numerical results, we find that there is no solution to the equation when $\eta < 0.4958$. So the cluster formed occasionally is unable to grow into a nucleation and the phase transition cannot take place when $\eta < 0.495$. When the volume fraction falls into a region of $\eta = 0.4958 \sim 0.4968$, the solution of Eq. (8) is k=3–12, so a small cluster composed of 3–12 spheres can grow into a nucleation and results in a phase transition. Obviously, the critical volume fraction denoting the phase transition of the united sphere system is $\eta_{\mathrm{c}} = 0.4958$. In fact, the experimental results show that in the system of monodisperse suspension, the critical volume fraction denoting phase transition from the colloidal fluid to a phase of fluid-crystal coexistence is 0.495.[3] In this case, the nucleation packing must have taken place. There is no solution to Eq. (8) when $\eta > 0.4968$. Therefore, our calculation result is in good agreement with the experimental results, and the reasonableness of the idea about the critical size for a cluster to nucleate is then verified. Furthermore, we emphasize the fact that all our discussions are strictly restricted within the framework CS state equation and no parameter is especially introduced externally as a modification factor. The results obtained in this paper are

just the natural conclusion of our theory.

However, we cannot confirm whether the cluster is packed into an fcc or a bcc or other structure. Obviously, if clusters consisting of the same number of spheres are packed into different structures, their densities are also different. So investigations in the cases of different cluster densities are needed. In this paper, beside the case of $\rho = 0.74$ discussed above, the cases for some other densities, such as $\rho = 0.64$, 0.60, 0.58, are also studied, and their results are listed in Table 1. From Table 1, it is known that both the critical volume fraction η and cluster size k are only slightly affected by the density ρ or the structure of the cluster: even the cluster density is changed from 0.74 to 0.58, the critical cluster size k remains at 3, and the critical volume fraction is changed only from 0.4958 to 0.4776. However, the structure of the cluster is significantly affected by the volume fraction η: when η changes from 0.4776 to 0.4958, the structure of the cluster changes from the random packed structure to cubic close-packed structure; the larger the volume fraction is, the more compactly can the cluster be packed.

Table 1. Critical volume fraction and critical size of the cluster for different densities.

ρ	0.74	0.64	0.60	0.58
η	0.4958–0.4968	0.4852–0.4862	0.4802–0.4812	0.4776–0.4786
k	3–12	3–38	3–18	3–30

From the above discussion it follows that though the critical size of the cluster is very small in a way, it plays a very important role in the theoretical analysis of cluster nucleation. When the critical cluster size is taken into consideration, the critical volume fraction denoting the phase transition can be determined without any parameter introduced externally. So the ideal about the critical size for cluster to nucleate shows more information about the nucleation packing. However, for simplicity, only the monodisperse suspension has been studied in this paper. Since the obtained result is good, the method discussed in this paper should be used to deal with a more complex system. So, for further studies, a binary colloidal system with a high asymmetry should be considered.

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