Critical volume fraction and critical size for a cluster to nucleate

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Abstract

Combined with the principle of entropy maximum and CS state equation, the critical size for a cluster to nucleate then the critical volume fraction of a phase transition is determined in this paper, and our result is in good agreement with the experiments. Furthermore, no parameter is introduced in the discussion. PACS: 82.70.Dd

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The phase behavior of a colloidal system is very complex and it has attracted considerable attentions all these years [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20]. 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, then a "cluster" consisting of the packed spheres turns out. 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 packed into a cluster so that the entropy of the system is increased. If the spheres are packed into many clusters at the same time, the packing takes place among these clusters rather than among other spheres. As a result, the cluster will turn to be a nucleation through the nucleation packing [15], and a phase transition turns out. However, in the packing process, there is a competing factor resulting entropy decreasing: when a part of large spheres pack together, the number of isolated spheres decreases resulting a decrease of entropy. So, there is a critical volume fraction for large spheres to pack together. Based on the entropy obtained by the CS state equation [16, 17], the critical volume fraction denoting the phase transition was determined, but the results is smaller than that obtained by experiments [13]. In fact, when the spheres are packed together, their excluded volumes are not completely overlapped, so a parameter was introduced to describe the packing degree in Ref. [14] and a better result was obtained. However, the parameter cannot be easily determined. It is very well if a good result can be theoretically obtained without any parameter. So we would like to reconsider the problem. In fact, it is known that, from a cluster to a phase transition, there is a long way to go. If the packing process is analyzed in more detail, we think that there is a critical size for a cluster to nucleate, i.e., only when the cluster is larger than the critical size, can it last for other spheres' further packing and grows larger and larger, then a phase transition turns out. Therefore, in the theoretical analyses, the critical size of the cluster should be included. Obviously, this will increase the complexity of the problem. To make the problem as simple as possible, a monodisperse suspension of hard-spheres is studied in this paper.

Supposing that there are N hard spheres of diameter ds in a container with a fixed volume V. As there are excluded volumes surrounding each sphere, the entropy of this system is closely related to the number of spheres and the free volume of the spheres Vf, and can be
written as \[14\]

\[ S = S(N, V_f), \]  

(1)

However, when \( k \) spheres pack into a cluster, which can be further taken as a large sphere, then the system turns to be 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 this binary colloidal system, two factors should be noted: one is that the number of the cluster keeps to 1 while the number of the isolated spheres decreases by \( k \); the other factor is that the size of the cluster increases with the increase of \( k \). For simplicity, the cluster consisting of \( k \) spheres is taken as a large sphere of diameter \( d_L \). Obviously, it is a function of \( k \), i.e., \( d_L = d_L(k) \). Then the entropy of this system can be rewritten as

\[ S = S(N_s, V_f, d_L(k)), \]  

(2)

and the variation of the entropy \( S \) is

\[ \delta S = \frac{\partial S}{\partial N_S} \delta N_S + \frac{\partial S}{\partial d_L} \frac{\partial d_L}{\partial N_S} \delta N_S \]  

(3)

where \( N_S = N - k \) is number of the isolated spheres.

Only when the expression of entropy \( S \) is known, can Eq. (3) be quantificationally studied. Fortunately, for a hard spheres system, the entropy can be analytically obtained through the generalize CS equation \[16, 17\]: for a binary mixture composed of \( N_L = c_L N \) large spheres with diameter \( d_L \) and \( N_S = c_S N \) small spheres with diameter (where \( c_S, c_L \) are concentrations of spheres satisfying \( c_S + c_L = 1 \)), the mean volume \( \omega \) and mean diameter \( d \) of a sphere have the following relation

\[ \omega = \frac{\pi}{6} (c_L d_L^3 + c_S d_S^3) = \frac{\pi}{6} d^3 \]

then the entropy is expressed as \[16, 17\]

\[ S_{hs} = S_{\text{gas}} + S_c + S_\eta + S_\sigma \]  

(4)

where

\[ S_{\text{gas}} = N k_B \ln(\epsilon \Omega \left( c_L m_L m_S^{c_S} \frac{2\pi k_B T}{\hbar^2} \right)^{3/2}) \]

\[ S_c = -N k_B (c_L \ln c_L + c_S \ln c_S) \]

\[ S_\eta = -N k_B (\varsigma - 1)(\varsigma + 3) \]
\[
S_\sigma = Nk_B \left( \frac{3}{2}(\varsigma^2 - 1)y_1 + \frac{3}{2}(\varsigma - 1)^2y_2 ight) \\
- \left( \frac{1}{2}(\varsigma - 1)(\varsigma + 3) + \ln \varsigma (1 - y_3) \right)
\]

Here \( \varsigma = V/N \) is the average volume of each sphere, \( m_L \) and \( m_S \) are the mass of a large and small spheres, and the parameters are defined as follow:

\[
\varsigma = (1 - \eta)^{-1} \\
y_1 = \frac{c_Lc_SD_L + d_S}{d^3}(d_L - d_S)^2 \\
y_2 = \frac{c_Lc_SD_Ld_i d_S(c_Ld_L^2 + c_Sd_S^2)(d_L - d_S)^2}{d^6} \\
y_3 = \frac{(c_Ld_L^2 + c_Sd_S^2)^3}{d^6}
\]

Here the constant \( e = 2.71828 \), the free volume fraction is \( 1 - \eta \). Except for the cases of higher densities and(or) larger diameter ratios of large-sphere to small-sphere, the validity of Eq.(4) is verified by numerical results.

In the system considered in this paper, we suppose that a cluster consisting of \( k \) spheres can be further taken as a large-sphere with mass \( m_L = km_S \) and diameter \( d_L = (\frac{6k}{\sqrt{2\pi}})^{1/3}d_S \), respectively. According to principle of entropy maximum, the critical volume fraction and critical size for a cluster to nucleate can then be obtained through the follow equation:

\[
\frac{dS}{dN_s} = \frac{\partial S}{\partial N_s} + \frac{\partial S}{\partial d_L} \frac{\partial d_L}{dN_s} = 0 \tag{5}
\]

where we have supposed the number of the small spheres is so large that \( N \rightarrow \infty \), then \( N_S \rightarrow \infty \), \( c_L \rightarrow 0 \), \( c_S \rightarrow 1 \), so

\[
\frac{\partial S}{\partial N_s} = k_B \left( \ln \frac{V}{N_S + 1} + \frac{3}{2}\ln \frac{2\pi c_S k_B T}{h^2} \right) \\
- k_B \left( \varsigma^2 + 2\varsigma - 3 \right) - \frac{\pi (N_S + 1)}{3V} k_B d_S^3 (\varsigma^3 + \varsigma^2) \tag{6}
\]

By the same way we also get:

\[
\frac{\partial S}{\partial d_L} = \frac{\partial S_{gas}}{\partial d_L} + \frac{\partial S_c}{\partial d_L} + \frac{\partial S_\eta}{\partial d_L} + \frac{\partial S_\sigma}{\partial d_L} \]

\[
= \frac{3\sqrt{2}k_B}{4d^2 S k} \left( \frac{6k}{\sqrt{2\pi}} \right)^{2/3} + \frac{\pi (N_S + 1)}{V} k_B d_L^2 \left( \varsigma^3 + \varsigma^2 \right) \\
+ k_B \left( \varsigma^2 + 2\varsigma - \ln \varsigma - 3 \right) \frac{\partial y_1}{\partial d_L} + \left( \varsigma^2 - \varsigma - \ln \varsigma \right) \frac{\partial y_2}{\partial d_L} \tag{7}
\]
\[ \frac{\partial y_1}{\partial d_L} = \frac{c_3 d_S^6 (3d_L + d_S) (d_L - d_S) d^6}{d^6} \]  
\[ \frac{\partial y_2}{\partial d_L} = \frac{c_3 d_S^6 (3d_L - d_S) (d_L - d_S) d^9}{d^9} \]  
\[ \frac{\partial d_L}{\partial N_S} = -\frac{d_S}{3} \left( \frac{6k}{\sqrt{2\pi}} \right)^{-2/3} \]  

Now we see that the relation between the volume fraction and the critical size of cluster \( k \) is described Eq.(5). Just like Ref. [14], we suppose that the diameter and mass of a small sphere are \( d_S = 6.9 \times 10^{-8} \text{m} \), and \( m_S = 3.2 \times 10^{-24} \text{Kg} \), and the temperature \( T = 300 \text{K} \). Then the relation between \( \eta \) and \( k \) is numerically determined, and the results are shown in Fig. 1 and Table I. From Fig.1, it is evident that the critical size for a cluster to nucleate decreases dramatically with the increase of the volume fraction, and it almost tends to zero when \( \eta = 0.50 \), so the critical volume fraction for a cluster to nucleate is no larger than 0.5. In addition, from table I, it is known that, when \( \eta = 0.492 \), the critical size for a cluster to nucleate is 1968; however, when \( \eta = 0.495 \), the critical size is 77; when \( \eta = 0.50 \), the critical size is only 9. In fact, we know that the possibility for 1968 spheres to pack into a cluster with \( \eta = 0.492 \) is less than that for 77 spheres to pack into a cluster with \( \eta = 0.495 \). So our result is reasonable. Combined with Fig. 1 and Table I, we get that the nucleation packing will take place when \( 0.495 < \eta < 0.50 \). On the other hand, in the system of monodisperse suspension of hard-spheres, the experimental results show that the critical volume fraction denoting phase transition from colloidal fluid to a phase of fluid and crystal in coexistence is 0.495[6]. Obviously, the phase transition takes place through the cluster’s nucleation packing. Therefore, our result is in good agreement with the experiment’s, and the reasonableness of the idea about the critical size for a cluster to nucleate is then verified.

However, there are two factors should be mentioned in our discussions: One is the cluster is cursorily treated as a large sphere. In fact, a cluster is not a large sphere. The other factor is about the validity of CS equation for a very dense system such as \( \eta = 0.495 \). Obviously, these two factors will affect our result in a way. We believe that our result can be slightly modified if a more accurate equation of state is used to deal with the nucleation packing. But the reasonableness of our model and the qualitative of our result cannot be changed by them completely. On the other hand, the reasonableness of our model will be further verified if a system with a high size asymmetry is considered. Because in this system the critical volume fraction will be very small in which the validity of CS equation is certain.
So, for further studies, the system with a high size asymmetry will be considered. From above discussion, we have shown that the critical size of the cluster is very important for nucleation packing. Taking the critical size into consideration, the critical volume fraction denoting a phase transition can be determined without any parameter. Compared with the model discussed in Ref. [14], in which a parameter was introduced to modify the packing process, the ideal about the critical size for cluster to nucleate shows more information about the nucleation packing.

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Table I. The critical volume fraction and the corresponding critical size for cluster to nucleate.

| Volume fraction η | 0.492 | 0.493 | 0.494 | 0.495 | 0.496 | 0.497 | 0.498 | 0.499 | 0.50  |
|-------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Cluster size k    | 1968  | 430   | 160   | 77    | 43    | 27    | 18    | 12    | 9     |

FIG. 1: The relation between the critical volume fraction η and the critical size of the cluster k.