

## Entropy-driven phase transition in binary mixtures

Chang-ming Xiao, Guo-jun Jin, Xiao-dong Shi, and Yu-qiang Ma\*

National Laboratory of Solid State Micro-structures, Nanjing University, Nanjing 210093, China

(Received 27 December 2000; published 13 June 2001)

Based on the principle of entropy maximum, a transparent method to study the phase separation is proposed. The excluded volume effects of binary mixtures of hard spheres with two different diameters are analyzed and the role of entropy is emphasized. As a result of the entropy variation caused by the packing of large spheres, there is a critical volume fraction to denote the phase boundary. It is shown that the variation of free volume fraction is influenced by the ratio  $\alpha = d_L/d_S$  of large to small sphere diameters and the ratio  $x = \eta_L/(\eta_L + \eta_S)$  of large-sphere volume fraction to the total volume fraction of large- and small-spheres. We introduce a modification factor  $\beta$  to describe the overlap degree of two large spheres excluded volumes when they pack together. The critical volume fractions for large-sphere packing with different values of  $\alpha$  and  $x$  are calculated, and the corresponding phase boundaries are determined. Our results are in quite good agreement with previous experimental measurements.

DOI: 10.1103/PhysRevE.64.011402

PACS number(s): 82.70.Dd, 64.60.Cn, 64.70.-p, 65.40.Gr

Suspensions of spherical colloidal particles in solvents have attracted considerable attention because of their rich thermodynamic properties and their industrial and medical utilities. Experimentally, it has been observed that, with increasing sphere concentration, there is a progression from colloidal fluid to a phase of fluid and crystal in coexistence, and to a fully crystallized phase [1–6]. The computer simulations with Monte Carlo and molecular dynamics methods also predicted so [7]. Theoretically, colloidal particles may be considered as hard spheres, therefore, systems consisting of hard spheres are very important. The well-known equation of state due to Carnahan and Starling (CS) [8] has usually been used to calculate phase diagrams of binary hard-sphere mixtures with modifications such as the small spheres resided in a reduced volume, which depends on the volume fraction of the large spheres. The equilibrium conditions are involved in the chemical potentials as well as osmotic pressures of large and small spheres. The reduced volume can be determined by the geometric argument [2], or by comparison of the chemical potentials of small spheres in an ideal gas with that in a binary hard-sphere fluid under Percus-Yevick approximation [9]. But all these theoretical results are lower than the experimental measurements [2]. Recently, Velasco *et al.* [10] have given the phase diagram of a binary mixture of hard spheres through a first-order perturbation theory and the agreement with computer simulations is good. To discuss the subject of hard-sphere packing caused by the excluded volume effects, or “depletion” force, however, we are going to study the problem in a new approach. Our approach will pay much attention to entropy of hard-sphere systems. Since the diameters of large and small spheres have been included in a theory [11], which is a generalization of the CS equation from pure fluids to mixtures of hard spheres, the effect of free volume on free energy or entropy can be studied directly, and the phase diagrams can be determined by entropy.

As is well known, the excluded volume plays an important role for systems consisting of hard spheres, because the free energies of these systems are entropy dominant, and the

entropy is related to the volume accessible to hard spheres. In a binary suspension of hard spheres with two different diameters,  $d_L$  and  $d_S$ , for the large and small spheres, respectively, the center of mass of a small sphere cannot penetrate within  $d_S/2$  away from a large-spheres’ surface, so there is a region of “excluded volume” surrounding each of large spheres. When the surfaces of two large spheres come near each other within a small-spheres’ diameter or the large spheres contact with the wall of container, the excluded-volume regions overlap, as shown in Fig. 1, so that the volume accessible to the center of mass of a small spheres, increases and the total entropy of the system also increases. However, the large spheres do not pack when the concentration of the system is low. In fact, there exists a critical concentration above which the colloid varies from the fluid phase to a coexisting phase of fluid and solid, and the sphere packing takes place.

In this paper, we study the binary mixtures of large- and small-hard spheres by entropy and find out the critical concentration or its corresponding volume fraction, and then some concrete examples will be given for large-sphere packing in several special cases. Furthermore, the factors that may affect the critical volume fraction, such as the ratio between large- and small-sphere diameters, and the ratio between their volume fractions, are discussed.

We consider a container with a fixed volume  $V$ . In the container there are large- and small-hard spheres with diameters  $d_L$  and  $d_S$ , respectively. Generally speaking, the en-

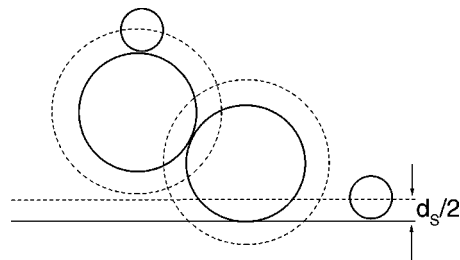


FIG. 1. Schematic diagram for excluded volume effect. The center of each small sphere is excluded from a layer of thickness  $d_S/2$  around a larger sphere and along the wall of the container.

\*Author to whom correspondence should be addressed.

entropy  $S$  of this binary system consisting of hard spheres is closely related to the numbers of large and small spheres ( $N_L$  and  $N_S$ ), the free volume  $V_f$ , and the temperature  $T$ , so that it can be written as

$$S = S(N_L, N_S, T, V_f). \quad (1)$$

It is reasonable to assume that the small spheres do not pack together, thus the number  $N_S$  of small spheres does not change, whenever the large spheres aggregate or not. Obviously, when a part of the large spheres has packed together, the number  $N_L$  of isolated large spheres decreases and the free volume  $V_f$  for small spheres will have an increment. If the temperature is invariable, the variation of the entropy  $S$  can be written as

$$\delta S = \frac{\partial S}{\partial N_L} \delta N_L + \frac{\partial S}{\partial V_f} \delta V_f = \left( \frac{\partial S}{\partial N_L} + \frac{\partial S}{\partial V_f} \frac{dV_f}{dN_L} \right) \delta N_L. \quad (2)$$

According to the second law of thermodynamics, any hard-sphere system must evolve in order to make its entropy maximum. In Eq. (2), when  $[\partial S/\partial N_L + (\partial S/\partial V_f)(\partial V_f/\partial N_L)] > 0$ , the large spheres do not pack together because the decrease of entropy caused by the variation  $\delta N_L$  due to large-spheres' packing dominates over the entropy increment caused by the increase of the free volume,  $\delta V_f$ . However, when  $[\partial S/\partial N_L + (\partial S/\partial V_f)(\partial V_f/\partial N_L)] < 0$ , the case is just the opposite, the large spheres tend to pack because the entropy contribution from the increase of the free volume due to large-spheres' packing plays a leading role. The critical case happens when  $\delta S/\delta N_L = 0$ . Therefore, there exists a critical number  $(N_L)_c$  of large spheres for the system. Since the volume of the container is assumed to be fixed, the volume fraction  $\eta$  can be ascertained if the number of hard spheres  $N (= N_L + N_S)$  is known, so the variation of entropy  $S$  with  $N$  is actually equivalent to its variation with the free volume fraction.

Equations (1) and (2) are useful for us to analyze the problem of sphere packing qualitatively and to predict the relation between entropy and free volume. In order to analyze the problem more exactly, we are going to deal with it quantitatively from the number of spheres through the generalized CS equation [11]. In 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  $d_S$  (where  $c_L, c_S$  are concentrations of spheres satisfying  $c_L + c_S = 1$ ), the mean volume  $\omega$  and mean diameter  $d$  of a sphere have the following relation

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

Mansoori *et al.* [11] provided a convenient and accurate thermodynamic description of the above system and, in particular, derived an expression for the Helmholtz free energy  $F_{hs}$ , and then Umar *et al.* [12] gave the corresponding expression for the total entropy  $S_{hs}$ , which is divided into four parts as

$$S_{hs} = S_{gas} + S_c + S_\eta + S_\sigma, \quad (3)$$

with

$$S_{gas} = Nk_B \ln \left[ e \Omega \left( e m_L^{c_L} m_S^{c_S} \frac{2\pi k_B T}{h^2} \right)^{3/2} \right],$$

$$S_c = -Nk_B (c_L \ln c_L + c_S \ln c_S),$$

$$S_\eta = -Nk_B (s-1)(s+3),$$

and

$$S_\sigma = Nk_B \left\{ \frac{3}{2} (s^2 - 1) y_1 + \frac{3}{2} (s-1)^2 y_2 - \left[ \frac{1}{2} (s-1)(s-3) + \ln s \right] (1-y_3) \right\},$$

where  $\Omega = V/N$  is the average volume of each sphere,  $m_L$  ( $m_S$ ) is the mass of a large (small) sphere, and the parameters are defined as follows:

$$s = (1 - \eta)^{-1}, \quad (4)$$

$$y_1 = \frac{c_L c_S (d_L + d_S)(d_L - d_S)^2}{d^3},$$

$$y_2 = \frac{c_L c_S d_L d_S (c_L d_L^2 + c_S d_S^2)(d_L - d_S)^2}{d^6},$$

and

$$y_3 = \frac{(c_L d_L^2 + c_S d_S^2)^3}{d^6}.$$

Here we define the constant  $e = 2.71828$ , the volume fraction  $\eta = \omega/\Omega$ , and thus the free volume fraction  $1 - \eta$ . It is easy to show that  $y_1 + y_2 + y_3 = 1$ .

The correctness of Eq. (3) has been tested by the molecule dynamics and Monte Carlo simulations, and also by the experimental results for liquid alloys [12–14]. It was found to be in good agreement with numerical results except for the cases of the higher densities and/or for larger diameter ratios. In higher small-sphere concentrations, this significant deviation may be caused by the changes of geometry packing where the larger spheres are not close packed, due to the oscillatory behavior of the entropic interactions, as shown in recent experimental results [13]. Obviously, the entropy  $S$  varies with the number  $N_L$ , the concentrations  $c_L, c_S$ , the volume fraction  $\eta$  (or the free volume fraction  $1 - \eta$ ), the diameters  $d_L, d_S$ , masses  $m_L, m_S$ , and temperature  $T$  of the hard-sphere system, but the relation between them is very complex, so we would try to solve it numerically.

We first discuss the variation of the free volume fraction  $(1 - \eta)$ , caused by large-sphere packing, which by definition, leads to

$$\frac{\delta(1 - \eta)}{\delta N_L} = -k'_1 \eta, \quad (5)$$

TABLE I. Measured and calculated volume fractions of the phases at equilibrium.

Sample	$d_L(\mu\text{m})/d_S(\mu\text{m})$	Modification	Measured $\eta_L^{msur}/\eta_S^{msur}$	Calculated $\eta_L^{calc}/\eta_S^{calc}$
1	$\alpha=0.460/0.069$	$\beta=0.63$	$(0.0556\pm 0.0054)/(0.1798\pm 0.0059)$	0.05559/0.16801
2	$=6.7$		$(0.0251\pm 0.0019)/(0.1893\pm 0.0020)$	0.02511/0.19551
3			$(0.01719\pm 0.00066)/(0.1970\pm 0.00022)$	0.01718/0.20367
4			$(0.0087\pm 0.0013)/(0.2168\pm 0.0026)$	0.00869/0.21311
5	$\alpha=0.605/0.069$	$\beta=0.60$	$(0.00709\pm 0.00086)/(0.2204\pm 0.0024)$	0.00702/0.21932
6	$=8.8$		$(0.0120\pm 0.0013)/(0.2106\pm 0.0026)$	0.01206/0.21121

where

$$k'_1 = \frac{d_L^3}{c_L d_L^3 + c_S d_S^3}. \quad (6)$$

From Fig. 1, it is evident that only some excluded volume of two large spheres overlaps when they pack together, and the free volume released is diameter dependent. In order to locate a liquidus curve where a binary liquid coexists with a dense solid of large spheres, Eq. (5) should be modified. As a first step toward this goal, we introduce a modification factor  $\beta$  in Eq. (5) to effectively take into account the change of the overlap region due to the large-sphere packing, i.e.,

$$\frac{\delta(1-\eta)}{\delta N_L} = -\beta k'_1 \eta = -k_1 \eta \quad (7)$$

with

$$k_1 = \beta k'_1 = \beta \frac{d_L^3}{c_L d_L^3 + c_S d_S^3}, \quad (8)$$

where the factor  $\beta$  stands for the degree of the overlap, therefore, it is concerned with the diameters  $d_L$ ,  $d_S$  and the concentrations  $c_L$ ,  $c_S$ .

For further discussion, we make a transformation on  $\Omega$  via Eq. (4), and have  $\Omega = \omega s / (s - 1)$ . The liquidus curve is determined by the condition  $(\delta S_{hs} / \delta N_L) = 0$ , which leads to

$$\begin{aligned} & 2k_1 y_3 s^3 + [(1+k_3)y_3 + 3k_1 y_2] s^2 + [2(1+k_3)y_3 \\ & + 3(1+k_2)y_2 - 3k_1(y_2 + y_3) + k_1] s \\ & - (1+k_3)y_3 \ln s + \ln(s-1) \\ & = \ln \left[ e \omega \left( e m_L^{c_L} m_S^{c_S} \frac{2\pi k_B T}{h^2} \right)^{3/2} \right] + \frac{3}{2} c_S \ln \frac{m_L}{m_S} - \ln c_L \\ & + [3(1+k_2)y_2 + 3(1+k_3)y_3 - k_1 y_3 + k_1] - 1, \quad (9) \end{aligned}$$

where

$$k_2 = \frac{c_S - c_L}{c_L} + \frac{c_S(d_L^2 - d_S^2)}{c_L d_L^2 + c_S d_S^2} - \frac{2c_S(d_L^3 - d_S^3)}{c_L d_L^3 + c_S d_S^3},$$

and

$$k_3 = \frac{3c_S(d_L^2 - d_S^2)}{c_L d_L^2 + c_S d_S^2} - \frac{2c_S(d_L^3 - d_S^3)}{c_L d_L^3 + c_S d_S^3}.$$

In principle, we can obtain a relation  $s = (c_L, d_L, d_S, T, m_L, m_S)$  from the equations above. But the analytic expression is very difficult to get, so we try to deal with this problem by numerical calculations. From Eq. (9), it is obvious that the temperature, the masses, and the diameters of hard spheres can affect the critical value.

As a first example, we consider the case in which the volume fractions of the two kinds of spheres are nearly equal, i.e.,  $\eta_L \approx \eta_S$ , where  $\eta_L = \pi c_L d_L^3 / 6\Omega$  and  $\eta_S = \pi c_S d_S^3 / 6\Omega$  are the volume fractions of larger and small spheres, respectively. If we define the parameters  $\alpha = d_L / d_S$  and  $x = \eta_L / (\eta_L + \eta_S)$ , the concentration  $c_L$  can be expressed as  $c_L = x / [\alpha^3(1-x) + x]$ . Let us take the diameter and mass of a small sphere being  $d_S = 6.9 \times 10^{-8}$  m and  $m_S = 3.2 \times 10^{-24}$  kg, respectively. These two parameters are in accordance with the polystyrene sphere in the experiment by Dinsmore *et al.* [2]. It is usual that the large and small spheres are all made of the same material, i.e., both have the same mass density, so  $d_L = \alpha d_S$  and  $m_L = \alpha^3 m_S$ . Take  $\alpha = 3$ ,  $\beta = 1.0$ , and the temperature  $T = 300$  K, the solution of Eq. (9) is  $s_c \approx 1.5827$ , therefore,  $\eta_c \approx 0.3682$ . This value is closely fitted to the experimental value  $\eta = \eta_L + \eta_S = 0.18$

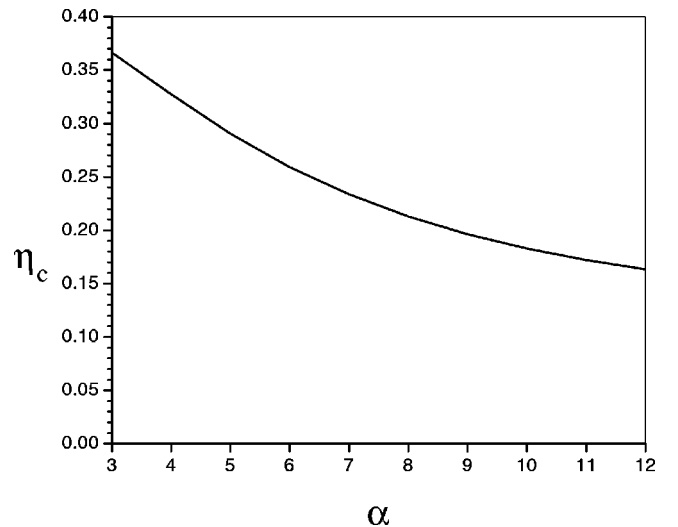


FIG. 2. The critical volume fraction  $\eta_c$  vs the ratio  $\alpha$  of the large- to small-sphere diameters at  $T = 300$  K.

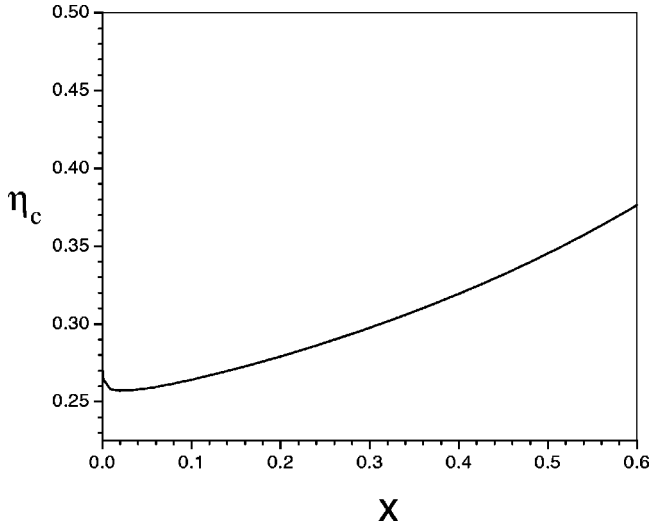


FIG. 3. The critical volume fraction  $\eta_c$  vs the ratio  $x = \eta_L/(\eta_L + \eta_S)$ .

+0.19=0.37. Consider the variation of temperature, when  $T=280$  K, the solution of Eq. (9) is  $\varsigma_c \approx 1.5818$  and  $\eta_c \approx 0.3678$ , and if the temperature is changed to be  $T=320$  K,  $\varsigma_c \approx 1.5836$ , and  $\eta_c \approx 0.3685$ . This means that the critical volume fraction is hardly affected by the temperature, i.e., it is nearly independent of temperature just as the observation in laboratory [2].

For the other two examples  $\alpha=6.7$  and  $\alpha=8.8$ , we take the modification factor of free volume fraction  $\beta=0.63$ ,  $0.60$ , respectively, and obtain the solutions of Eq. (9) with different values of  $x$ . The numerical results are listed in Table I, in which we also cited the experimental measurements from Ref. [2]. The total volume fraction in fluid phase measured and calculated are  $\eta_L^{msur} + \eta_S^{msur}$  and  $\eta_L^{cal} + \eta_S^{cal}$ , where the superscript *msur* and *cal* denotes the measured and calculated value in the fluid phase at equilibrium, respectively. From Table I, it is clear that our calculations are in good agreement with the experiments. We note that the modification factor  $\beta$  decreases as the ratio  $\alpha$  increases. This is due to the fact that when two large spheres pack together, the overlap degree of their excluded volume will decrease remarkably as the ratio  $\alpha$  increases. However, the manner that  $\beta$  changes with  $\alpha$  will become very complex when  $\eta_L \gg \eta_S$  or  $\eta_L \ll \eta_S$ .

To see more clear that the critical volume fraction is affected by the ratio  $\alpha$ , we deal with the case  $\eta_L = \eta_S$ . Indeed, as the ratio  $\alpha$  increases, the excluded volume effect will become more and more evident and the critical volume fraction will decrease. This argument has been confirmed by the experimental results [2]. It is interesting to find out whether our scheme can predict this behavior. The numerical calculation of Eq. (9) does tell us that the critical volume fraction becomes lower as the ratio  $\alpha$  of the large- to small-sphere diameters increases. This tendency is perfectly described in Fig. 2. In the present case, we can approximately fit an expression

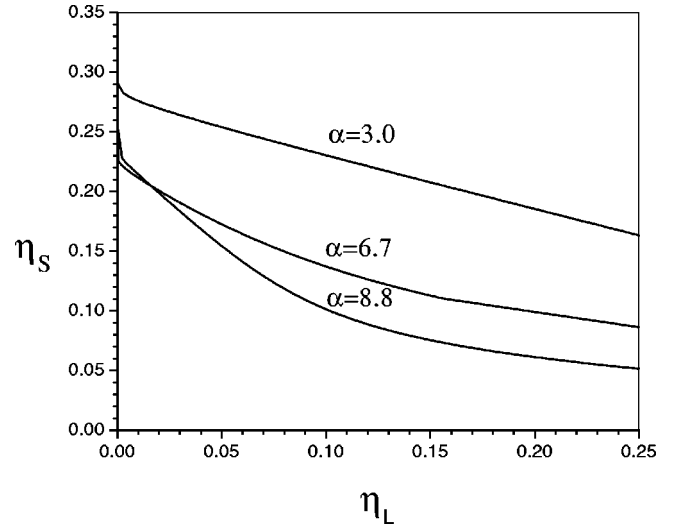


FIG. 4. Phase diagrams for different values of  $\alpha$ .

$$\beta = 1 - \frac{\alpha - 3}{2(\alpha - 10) + 17}.$$

We now turn to consider the effect of the ratio  $x$  on the critical volume fraction for different values of  $\alpha$ . For  $\alpha=3.0$ , the numerical results for the relation between  $\eta_c$  and  $x$  are plotted in Fig. 3. We see from Fig. 3 that the critical volume fraction increases as the ratio  $x$  increases. This indicates that it is more difficult for large sphere to pack as the small sphere volume fraction decreases. The phase diagrams for  $\alpha=3.0$ ,  $6.7$ , and  $8.8$  have also been plotted in Fig. 4. Obviously, below the liquidus curve, no sphere packs, while above it, packing takes place. From Fig. 4, on the other hand, we see that the liquidus curve of  $\alpha=8.8$  is higher than that of  $\alpha=6.7$  when  $\eta_L \rightarrow 0$ . This singularity is consistent with the measurements listed in Table I. Our results are exactly fitted to the experiments in Ref. [2], so the excluded volume effect and entropy approach can be used to describe the sphere packing and the phase separation of binary colloids.

In summary, we have studied the hard-sphere packing of binary mixtures by starting from an entropy formulation. From the discussion above, we have shown that the excluded volume plays an important role in systems consisting of binary hard spheres. As the overlap degree of the excluded volume varies with the ratio  $\alpha$  and  $x$ , we have introduced a modification factor  $\beta$ , to describe the variation of the free volume. This variation of the free volume leads to an entropy force to drive a phase transition from liquid to a coexisting phase of liquid and solid. By numerical calculations, we have shown that there is a critical volume fraction for the excluded volume effect, and phase boundaries can be correctly determined. Our approach is transparent and the results are in good agreements with the experiments.

This work was supported by the National Natural Science Foundation of China under Grants No. 19925415 and No. 19847003 and the ‘‘Climbing Project’’ of the National Commission of Science and Technology of China.

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