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Description of concentration fluctuations in liquid binary mixtures with nonadditive potentials

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The segregation or phase separation in a binary mixture is investigated within a quasilattice model and the hard-sphere-like model. The hard-sphere results are improved by incorporating a nonadditive attractive tail interaction. An analytic expression for the concentration fluctuation $S_{cc}(0)$ is obtained for the Lennard-Jones system and its equivalence to the lattice-based model is established. The results suggest that the segregation or phase separation, with either model, is an outcome of the energetic effect.

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I. INTRODUCTION

The atomic correlations in a binary mixture leading to homocoordination (preference for like atoms to pair as nearest neighbors) and heterocoordination (preference for unlike atoms to pair as nearest neighbors) strongly influence the phase stability of the system. It helps to analyze the phase separation and the compound forming tendencies in binary liquid mixtures. In recent years, a considerable effort has been made (for example, see Refs. [1–4] to identify the physical reasons responsible for phase separation either in terms of interatomic forces or in the light of entropic and enthalpic contributions to the free energy.

Here we intend to address it by considering the concentration fluctuations $S_{cc}(0)$ [5] in the long wavelength limit and by using the simplest possible models for mixture, namely, the quasilattice model and the hard-sphere model. The phase separation is signaled by a strong enhancement of $S_{cc}(0)$ which diverges as the spinodal is approached. In the approach of quasilattice theory, it has become possible to investigate the role of entropic and enthalpic effects on phase separation in binary mixture. The results suggest that the segregation in a binary mixture is an outcome of the enthalpic contribution where the system is dominated by repulsive interactions, i.e., a positive value for the interchange energy. The interchange energy (ω) is so defined that if we start with two pure species 1 and 2, and exchange an interior 1 atom with an interior 2 atom, the change in energy of the system is 2ω. With a view to obtaining greater physical insight, we have also considered the problem of segregation within the framework of an entirely different approach based on the hard-sphere model. The latter is improved upon with nonadditive tail interactions for unlike pairs and hence an analytic expression for $S_{cc}(0)$ is obtained. Such a correction for finite tail interactions is largely responsible for the divergence in the $S_{cc}(0)$. The results that are obtained via these two different approaches are quite complementary to each other.

The approximations and the observations that are made for the quasilattice model are presented in Sec. II. In Sec. III, the usual hard-sphere model of a binary mixture is modified for nonadditive tail interactions, and an analytic expression for $S_{cc}(0)$ is obtained. The impact of potentials on mixing behavior is critically examined. We follow with a small Sec. IV dealing with the concluding remarks.

II. QUASILATTICE APPROACH FOR ENTROPIC AND ENTHALPIC CONTRIBUTIONS TO PHASE SEPARATION IN BINARY LIQUID MIXTURE

Let one mole of the mixture be made isothermally from the pure components; then the Gibbs free energy of mixing is expressed as

$$\Delta G = -T\Delta S + \Delta H \ , \tag{2.1}$$

where the first term on the right-hand side (rhs) represents the entropic contribution while the second term is due to enthalpic effects. All energetic effects of mixing are contained in ΔH. With a view to investigating the effect of the two contributions separately to $S_{cc}(0)$, we first propose to make use of the quasilattice theory (QLT) of liquid mixtures, which is based on the ideas underlying Guggenheim's [6] theory of mixtures of polymers. QLT allows one to write an explicit expression for ΔS and ΔH as follows.

Let the constituent atoms (1 and 2) of the binary mixture differ from one another in size and shape, with N_1 the number of atoms of species 1, i.e., N_1 occupy a group of γ_1 lattice sites and N_2 occupy γ_2 lattice sites. If there is no energetic effect (i.e., $\Delta H = 0$), then the entropy of mixing can be expressed [6] as

$$\begin{aligned}\frac{\Delta S}{Nk_BT} = {} & -C_1 \ln\left[\frac{C_1}{C_1+\gamma C_2}\right] - C_2 \ln\left[\frac{\gamma C_2}{C_1+\gamma C_2}\right] \\ & -\frac{1}{2}zq_1C_1 \ln\left[\frac{C_1+\gamma C_2}{C_1+qC_2}\right] \\ & -\frac{1}{2}zq_2C_2 \ln\left[\frac{C_2+C_1/\gamma}{C_2+C_1/q}\right] \ ,\end{aligned} \tag{2.2}$$

where k_B denotes the Boltzmann constant, $N\ (= \sum_i N_i)$ is the total number of atoms, $C_i (= N_i/N)$ are atomic concentrations, and $\gamma = \gamma_2/\gamma_1$. q is related to z (the coordination number) and γ as

$$\tfrac{1}{2} z(\gamma_i - q_i) = \gamma_i - 1, \qquad i = 1, 2. \tag{2.3}$$

Equation (2.2) simplifies considerably for $z \to \infty$, i.e., one finds for $\Delta G(z \to \infty)$,

$$\frac{\Delta G}{N k_B T} = -\frac{\Delta S}{N k_B T} = C_2 \ln \psi + C_1 \ln (1 - \psi) \ , \tag{2.4}$$

$$\psi = \frac{\gamma C_2}{C_1 + \gamma C_2} \ . \tag{2.5}$$

One can readily identify Eq. (2.4) as Flory's formula. Thus the concentration fluctuations in the long wavelength limit, $S_{cc}(0)$, due to entropic effects becomes

$$S_{cc}(0) = N k_B T \left(\frac{\partial^2 \Delta G}{\partial C_1^2} \right)^{-1}_{T,P,N} \tag{2.6}$$

$$= \frac{C_1 C_2}{1 + C_1 C_2 \left(\frac{\gamma - 1}{C_1 + \gamma C_2} \right)^2} . \tag{2.7}$$

For practical purposes, $\gamma = \gamma_2/\gamma_1 \equiv \Omega_2/\Omega_1$ (Ω is the atomic volume) can be regarded as the mismatch volume effect term,

$$S_{cc}(0) = \frac{C_1 C_2}{1 + C_1 C_2 \frac{(\Omega_2 - \Omega_1)^2}{\Omega_{\rm id}^2}} , \tag{2.8}$$

where

$$\Omega_{\rm id} = C_1 \Omega_1 + C_2 \Omega_2 \ . \tag{2.9}$$

If $\Omega_1 = \Omega_2$, then

$$S_{cc}(0) = S_{cc}^{\rm id}(0) = C_1 C_2 \ . \tag{2.10}$$

For $\Omega_1 \neq \Omega_2$, $S_{cc}(0)$ deviates from the ideal value. Any deviation of $S_{cc}(0)$ from the ideal value $S_{cc}^{\rm id}(0)$ is of great interest to anyone trying to visualize the degree of interaction in the mixture. If, at a given composition, $S_{cc}(0) \gg S_{cc}^{\rm id}(0)$, then there is a tendency for segregation (preference for like atoms to pair as nearest neighbors); $S_{cc}(0) \ll S_{cc}^{\rm id}(0)$ is an indication of heterocoordination (preference for unlike atoms to pair as nearest neighbors). The former is often interpreted as a signature of phase separation while the latter suggests the existence of chemical short-range order.

It is evident from Eq. (2.8) that $S_{cc}(0)$ is not symmetrical at $C = 0.5$: the position of asymmetry depends on Ω_2/Ω_1. But in no case is $S_{cc}(0)$ greater than $S_{cc}^{\rm id}(0)$, i.e., any positive deviation of $S_{cc}(0)$ from the ideal mixture is not determined by entropic effects.

On the other hand, if one considers the energetic effect of the binary mixture (i.e., $\Delta H \neq 0$) then QLT provides [6] an explicit expression for ΔH. Taking this effect into account, and in the limit $z \to \infty$, the expression for ΔG becomes

$$\frac{\Delta G}{N k_B T} = C_2 \ln \psi + C_1 \ln (1 - \psi) + C_1 \psi \left(\gamma_1 \frac{w}{k_B T} \right) , \tag{2.11}$$

where $w\ (= z[w_{12} - (w_{11} + w_{22})/2])$ is the interchange energy. w_{12}, w_{11}, and w_{22} are the energies for 1-2, 1-1, and 2-2 pairs of atoms, respectively. Obviously, if $w < 0$, there is a tendency to form unlike atom pairs, and if $w > 0$, the like atoms tend to pair together. $w = 0$, however, indicates that atoms in the mixture do not show preferential bonding of any type.

The first two terms on the rhs of Eq. (2.11) are due to entropic contributions and the last term arises from enthalpic effects. On substituting (2.11) into (2.6), one has

$$S_{cc}(0) = \frac{C_1 C_2}{1 - C_1 C_2 f(\gamma, W)} , \tag{2.12}$$

with

$$f(\gamma, W) = \frac{2\gamma^2 W - (\gamma - 1)^2 \{C_1 + \gamma C_2\}}{(C_1 + \gamma C_2)^3} , \tag{2.13}$$

$$W = \gamma_1 \left(\frac{w}{k_B T} \right) . \tag{2.14}$$

For $W \to 0$, Eq. (2.12) reduces to Eq. (2.7). On the other hand, for $\gamma \to 1$ (i.e., $\Omega_1 = \Omega_2$), one gets

$$S_{cc}(0) = \frac{C_1 C_2}{1 - C_1 C_2 \left(\frac{2W}{k_B T} \right)} , \tag{2.15}$$

i.e., $S_{cc}(0)$ is always symmetrical at $C = 0.5$. But unlike Eq. (2.8), it is now possible that $S_{cc}(0)$ is either greater than $S_{cc}^{\rm id}(0)$ or less than that. The positive and the negative deviations from the ideal mixture depend on the positive and negative values of the interchange energy (W). The general behavior of $S_{cc}(0)$ [i.e., Eq. (2.12)], after considering both the entropic and the enthalpic effect, is shown in Fig. 1, where $S_{cc}^{*}(0)\ [= S_{cc}(0)/S_{cc}^{\rm id}(0)]$ has been plotted for different values of γ and W, for an equiatomic binary mixture ($C_1 = C_2 = 0.5$). It is clear that for $W = 0$ (no enthalpic effects), $S_{cc}^{*}(0) \to 1$ (ideal mixture) for $\gamma \simeq 1.0$. With increasing values of the size ratio γ, $S_{cc}^{*}(0) < 1$, thereby indicating ordering in the mixture. Similarly, if $W < 0$, there is an order for all possible values of γ.

One obtains, however, $S_{cc}^{*}(0) > 1$, i.e., segregation for $W > 0$. It is interesting to observe that even for positive interchange energy, Eq. (2.12) suggests a crossover from the segregation to order if the mismatch volume term (γ) is large enough, indicating that the segregation in a binary mixture is an outcome of the enthalpic contribution.

III. ROLE OF INTERACTIVE POTENTIALS IN THE HARD-SPHERE-LIKE APPROACH TO PHASE STABILITY OF LIQUID MIXTURES

Since the early work by Lebowitz and Rowlinson [1] on hard-sphere mixtures of additive nature [$\sigma_{12} = (\sigma_{11} +$

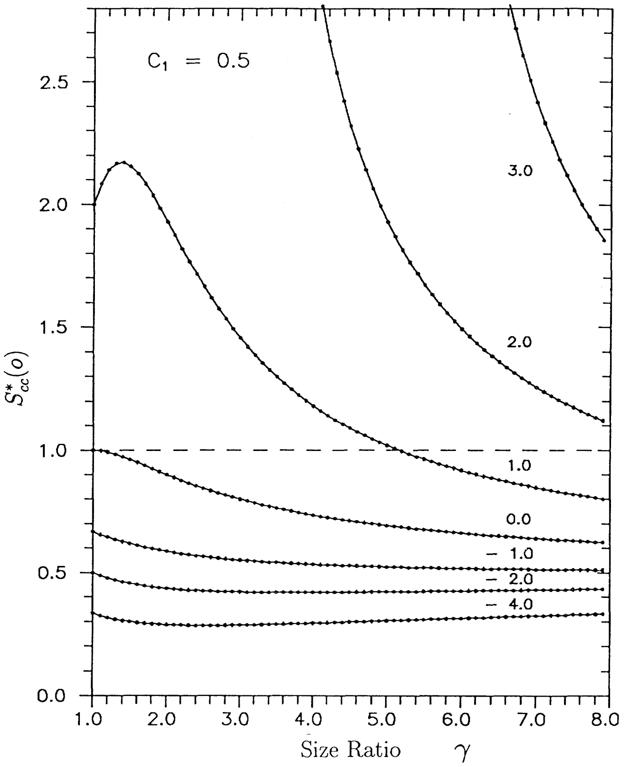

FIG. 1. Reduced $S^*_{cc}(0)$ [$= S_{cc}(0)/S^{\rm id}_{cc}(0)$] against size ratio γ at different exchange energies $W = -4.0, -2.0, -1.0, 0.0, 1.0, 2.0$, and 3.0 as calculated from Eq. (2.12).

$\sigma_{22})/2$, σ_{ij} are hard-sphere diameters], it is well known that at least within the Percus-Yevick (PY) approximation, hard spheres of arbitrary size ratio will mix in all proportions in the fluid phase. But recently the phase separation has been observed in soft-sphere mixtures [7, 8] in which the underlying effective hard-sphere mixture is characterized by nonadditive diameters, i.e., $\sigma_{12} > (\sigma_{11} + \sigma_{22})/2$. In this case the phase separation is noticed even at quite small size ratio $\gamma = \sigma_{22}/\sigma_{11}$, (where $\sigma_{22} > \sigma_{11}$).

In a quite recent letter, Biben and Hansen [9] used a numerical solution of the, so called, generalized PY approximation to obtain $S_{cc}(0)$ for dense hard-sphere mixtures. It predicts phase separation in a binary hard-sphere mixture if the size ratio $\gamma \geq 4.76$. This result is clearly of considerable interest. However, one may wonder to what extent phase separation in a hard-sphere mixture depends on the approximation that one used to compute the equation of state of such a mixture.

We present a simple but representative analytical expression for $S_{cc}(0)$ for binary Lennard-Jones (LJ) liquid mixtures, with additive hard-sphere diameter but nonadditive attractive tail interactions for unlike pairs. We begin by considering a binary mixture of N molecules in volume Ω of which N_1 molecules are of hard-sphere diameter σ_{11} and N_2 molecules of diameter $\sigma_{22} (\sigma_{22} > \sigma_{11})$. This gives a partial density $\rho_i = \frac{N_i}{\Omega}$ and packing fraction $\eta_i = \frac{\pi}{6}\rho_i\sigma_i^3, (i = 1, 2)$. The total density of the mixture is $\rho = \sum_i \rho_i$. Also, we assume that the constituent molecules are interacting via a pair potential $V_{ij}(r)$ which can be divided into a short-range repulsive (normally the hard-sphere potential) and long-range attractive contributions, i.e.,

$$V_{ij}(r) = V^{\rm hs}_{ij}(r) + V^T_{ij}(r) \quad (i, j = 1, 2). \tag{3.1}$$

The Helmholtz free energy F and the pressure P for the mixture can be easily expressed within the random-phase-approximation (RPA) scheme [10, 11]: the Gibbs free energy G becomes

$$G = F + \frac{P}{\rho} = G_{\rm hs} + G_T, \tag{3.2}$$

where

$$G_{\rm hs} = F_{\rm hs} + P_{\rm hs}/\rho, \tag{3.3}$$

$$G_T = \rho \sum_{i,j} C_i C_j \overline{V}^T_{ij}(0). \tag{3.4}$$

$F_{\rm hs}$ and $P_{\rm hs}$ refer to the Helmholtz free energy and pressure of the hard-sphere mixture, respectively, and

$$\overline{V}^T_{ij}(0) = 4\pi \int_{\sigma_{ij}}^{\infty} dr r^2 V^T_{ij}(r).$$

Finally, $S_{cc}(0)$ can be calculated via the standard relation [see Eq. (2.6)]. This leads to

$$S_{cc}(0)^{-1} = S^{\rm hs}_{cc}(0)^{-1} + S^T_{cc}(0)^{-1}. \tag{3.5}$$

Equation (3.5) is the RPA result for $S_{cc}(0)$ which is general and easy to use once reliable expressions for the hard-sphere reference system are available and an accurate prescription is used to divide $V_{ij}(r)$ as in Eq. (3.1). For simplicity, we have selected a LJ potential,

$$V^{\rm LJ}_{ij}(r) = 4\epsilon_{ij}\left\{\left(\frac{\sigma_{ij}}{r}\right)^{12} - \left(\frac{\sigma_{ij}}{r}\right)^{6}\right\}, \tag{3.6}$$

where ϵ_{ij} represent the attractive potential depths, and we used the well known Weeks-Chandler-Anderson (WCA) [12–14] perturbation scheme to enable us to make such a division,

$$V^0_{ij}(r) = \begin{cases} V^{\rm LJ}_{ij}(r) + \epsilon_{ij}, & r \leq r^{\rm min}_{ij} \\ 0, & r \geq r^{\rm min}_{ij}, \end{cases} \tag{3.7}$$

$$V^T_{ij}(r) = \begin{cases} -\epsilon_{ij}, & r \leq r^{\rm min}_{ij} \\ V^{\rm LJ}_{ij}(r), & r \geq r^{\rm min}_{ij}, \end{cases} \tag{3.8}$$

$$\text{with} \qquad r^{\rm min}_{ij} = (2)^{\frac{1}{6}}\sigma_{ij}.$$

Here $V^0_{ij}(r)$, the reference potential, can be approximated to be $V^{\rm hs}_{ij}(r)$ if σ_{ij} are shown such that the blip function [13, 14] vanishes. This method provides σ_{ij}, which depend on both density and temperature. The detailed expressions for the hard-sphere reference mixture are available within the analytical solution of the PY approximation given by Lebowitz and Rowlinson [1].

By making use of Eqs. (3.2) and (3.3) and the $F_{\rm hs}$ and $P_{\rm hs}$ expressions given in Ref. [1] in Eq. (2.6), we obtain

$$S_{cc}^{\text{hs}}(0)^{-1} = \frac{1}{C_1C_2} + \frac{\pi\rho}{2}\left[\frac{9x^3d_3^2}{(1-\eta)^4} + \frac{18x^2d_2d_3 + 4xyd_3^2}{(1-\eta)^3} + \frac{9xd_2^2 + 4yd_1d_2 + 4xd_1d_3 + \left(\frac{\pi\rho}{18}\right)d_3^2}{(1-\eta)^2} + \frac{4d_1d_2}{(1-\eta)}\right], \qquad (3.9)$$

where $d_1 = \sigma_{11} - \sigma_{22}$, $d_2 = \sigma_{11}^2 - \sigma_{22}^2$, $d_3 = \sigma_{11}^3 - \sigma_{22}^3$, $y = \frac{\pi}{6}\rho\sum_i C_i\sigma_{ii}$, $z = \frac{\pi}{6}\rho\sum_i C_i\sigma_{ii}^2$, and $\eta = \frac{\pi}{6}\rho\sum_i C_i\sigma_{ii}^3$.

Similarly, by making use of Eqs. (3.2) and (3.4) in Eq. (2.6), we obtain for $S_{cc}^T(0)^{-1}$

$$S_{cc}^T(0)^{-1} = \frac{\rho K}{k_BT}\left\{(2-\eta)(D_1+D_2) - \frac{\pi\rho d_3}{3}(C_1D_1 - C_2D_2)\right\}, \qquad (3.10)$$

where $D_1 = \epsilon_{11}\sigma_{11}^3 - \epsilon_{12}\sigma_{12}^3$ and $D_2 = \epsilon_{22}\sigma_{22}^3 - \epsilon_{12}\sigma_{12}^3$. K is a constant to be obtained from an integral over the reduced interatomic separation $r^* = r/\sigma_{11}$,

$$K = 4\pi\int_o^\infty dr^* r^{*2} V_{11}^T(r^*). \qquad (3.11)$$

Equation (3.5), together with Eqs. (3.9) and (3.10), forms the required analytical expression for $S_{cc}(0)$ for our model. One of the prime objectives in expressing $S_{cc}(0)$ in the present form is that it can be used to investigate the role of hard-sphere diameters σ_{ij} and the potential well depths ϵ_{ij} separately.

In what follows we discuss some of the useful conditions supported by numerical results. For actual calculations we found it convenient to work in reduced units, for example, density $\rho^* = \rho\sigma_{11}^3$, temperature $T^* = k_BT/\epsilon_{11}$, pressure $P^* = P\sigma_{11}^3/\epsilon_{11}$, and $S_{cc}^*(0) = S_{cc}(0)/S_{cc}^{\text{id}}(0)$. We carried out our calculations for given values of $P^* = 3.0$ and $T^* = 2.0$, which typically correspond to normal pressure and temperature that are suited to the range of density of liquid metals. We investigate the effects of size ratio $\gamma (= \sigma_{22}/\sigma_{11})$, the energy ratio $\beta (= \epsilon_{22}/\epsilon_{11})$, and the interactive energy parameter $\alpha (= \epsilon_{12}/\sqrt{\epsilon_{11}\epsilon_{22}})$ on the phase separation or in the process of compound formation.

Case 1. Consider a binary mixture of hard spheres whose diameters and interaction energies are such that

$$\sigma_{11} = \sigma_{22} = \sigma_{12} \quad \text{and} \quad \epsilon_{11} = \epsilon_{22} = \epsilon_{12}, \qquad (3.12)$$

i.e., $\gamma = 1.0$, $\beta = 1.0$, and $\alpha = 1.0$. Then one readily sees that $d_1 = d_2 = d_3 = 0$ and $D_1 = D_2 = 0$. Equations (3.9) and (3.10) reduce, respectively, to

$$S_{cc}^{\text{hs}}(0)^{-1} = \frac{1}{C_1C_2}, \qquad (3.13)$$

$$S_{cc}^T(0)^{-1} = 0. \qquad (3.14)$$

Therefore, Eq. (3.5) implies

$$S_{cc}(0) = S_{cc}^{\text{id}}(0) = C_1C_2. \qquad (3.15)$$

Thus, Eq. (3.12) sets the sufficient conditions for a binary hard-sphere mixture to be ideal.

Case 2. In order to see the effect of the mismatch of the sizes of hard spheres on mixing, we assume that there is no change of energetics, i.e., $\beta = \alpha = 1.0$ and $\gamma \neq 1.0$.

$$\epsilon_{11} = \epsilon_{22} = \epsilon_{12} \quad \text{and} \quad \sigma_{11} \neq \sigma_{22}. \qquad (3.16)$$

$S_{cc}(0)$ is calculated from Eq. (3.9) for different values of size ratio $\gamma = 1.0$, 1.25, 1.5, 2.0, and 3.0. The results are shown in Figs. 2(a) and 2(b), where $\gamma = 1.0$ corresponds to ideal values. With the increase of size ratio, the values of $S_{cc}^*(0)$ decrease rapidly from the ideal value 1 exhibiting an ordered state. The larger the values of γ, the more ordered a state is achieved in the mixture. For $\gamma > 2.0$ a flat minimum is observed over a wide range of concentrations. This suggests that the degree of order is quite similar for all possible compositions of the binary mixture.

It is interesting to see that $S_{cc}^*(0)$ cannot be greater than 1 for any size effect. Thus, in the absence of energetic effects, any mismatch size ratio cannot bring segregation in a binary mixture. This is consistent with what we observed for quasichemical theory in Sec. I.

Case 3. Finally, we investigated the role of interactive potential on mixing which appears in our formation through the Gibbs function G_T. In that case, both $S_{cc}^{\text{hs}}(0)$ and $S_{cc}^T(0)$ contribute to total $S_{cc}(0)$. Let the attractive tail for unlike atoms be nonadditive, i.e.,

$$\epsilon_{12} = \alpha(\epsilon_{11}\epsilon_{22})^{\frac{1}{2}}. \qquad (3.17)$$

The nonadditive parameter α plays an important role in the mixing behavior of a binary mixture. The impact of α for a particular case ($\gamma = 1.0, \beta = 1.0$) is shown in Fig. 3. $\alpha = 1.0$ corresponds to ideal value. $S_{cc}^*(0)$ is always symmetrical at C = 0.5. The segregation occurs $[S_{cc}^*(0) > 1.0]$ for $\alpha < 1.0$. With decreasing α, the range of compositions, in which the segregation is expected, widens considerably. A good degree of order is found to prevail over a wide range of concentrations for comparatively large α ($\alpha > 1.0$). It is not only the nonadditive parameter α which controls the segregation. The latter depends very much on the values of the well depth (ϵ_{11} or ϵ_{22}) of the constituent species. In order to demonstrate this, we take $\gamma = 1.0$, $\alpha = 1.0$, and $\beta = 1.0$, 1.5, 2.0, 2.5, 3.0, and 5.0 to calculate $S_{cc}^*(0)$. The results are depicted in Fig. 4(b). $S_{cc}^*(0)$ is always greater than the ideal value, i.e., 1.0. For large differences of well depths ($\beta \gg 1.0$) segregation results quite easily even with $\alpha = 1.0$. Any deviation of the value of α from $\alpha = 1.0$ affects the mixing characteristic considerably. The results obtained for $\alpha = 0.8$ are demonstrated in Fig. 4(a). Again for all values of well depth ratio $\beta = 1.0$, 1.5, 2.5, and 5.0, $S_{cc}^*(0) > 1.0$. This result is qualitatively similar in nature to that with $\alpha = 1.0$. It should be noted, however, that by lowering the value of $\alpha \leq 1.0$, the segregation effect is enhanced to a great extent for larger mismatch well depths, and the mixture undergoes phase separation.

The results for $\alpha \geq 1.0$ (e.g., $\alpha = 1.2$) are depicted in Fig. 4(c). $S_{cc}^*(0)$ in this case is both greater and smaller than the ideal values. That is to say, the segregation or

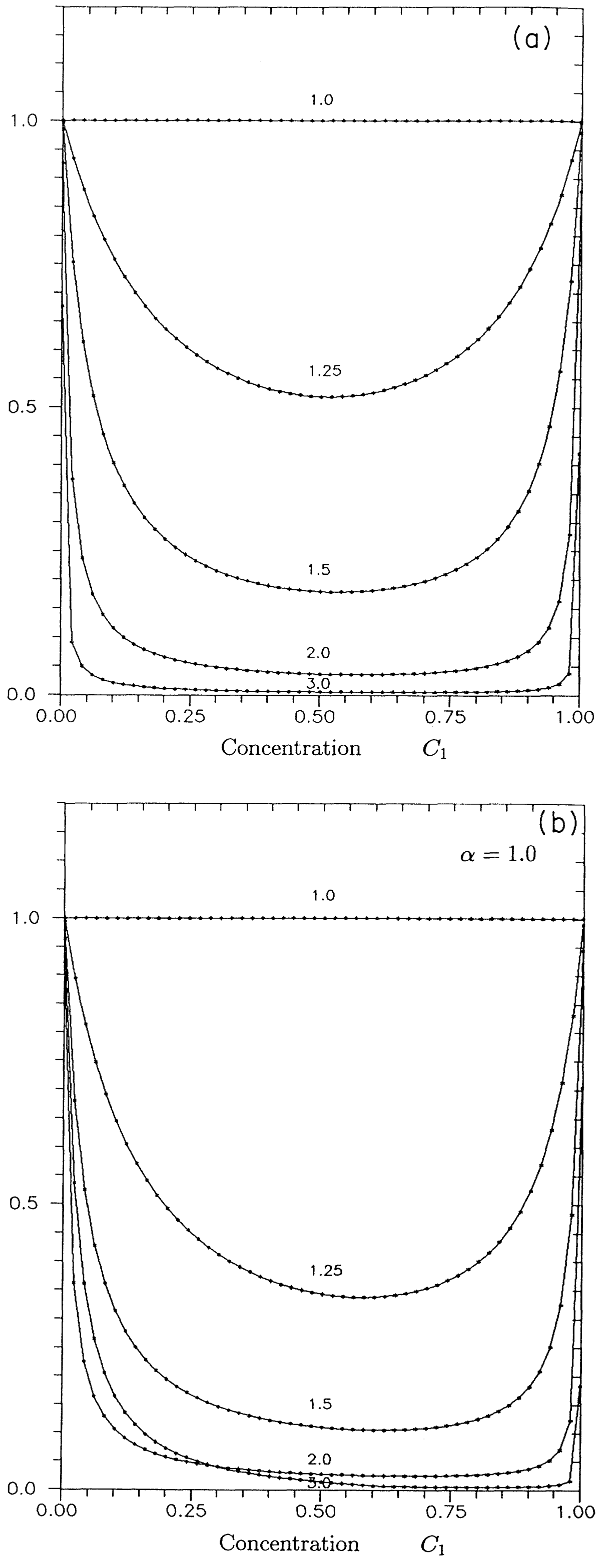

FIG. 2. The reduced $S^*_{cc}(0)$ vs concentration of a binary mixture at different size ratios γ =1.0, 1.25, 1.5 2.0, and 3.0. (a) Hard-sphere mixture with $\epsilon_{11} = \epsilon_{22} = \epsilon_{12} = 0$. (b) Modified hard-sphere results for Lennard-Jones potentials with energy ratio $\beta = \epsilon_{22}/\epsilon_{11} = 1.0$ and the interaction energy parameter $\alpha = 1.0$.

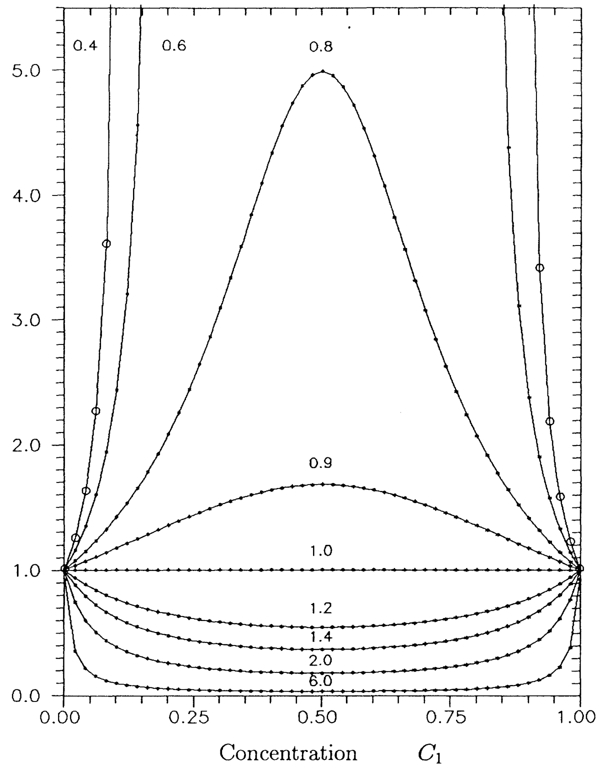

FIG. 3. Reduced $S^*_{cc}(0)$ vs concentration of binary mixture of size ratio $\gamma = 1.0$ and energy ratio $\beta = 1.0$ with different interaction energy parameters α = 0.4, 0.6, 0.8, 0.9, 1.0, 1.2, 1.4, 2.0, and 6.0.

order occurs depending upon the mismatch of the well depths [15–17].

IV. CONCLUDING REMARKS

The mixing behavior of a binary mixture with a particular reference to segregation or phase separation is discussed in the light of quasilattice theory and the hard-sphere-like approach. The latter approach is improved by appending nonadditive tail interactions for unlike pairs. An analytical expression for $S_{cc}(0)$ is obtained for both the quasilattice model and the hard-sphere model which is amended with Lennard-Jones attractive interactions. The main results of the present work are as follows.

(a) The interchange energy (w) of the quasilattice model and the well depth (ϵ_{ij} with interactive parameter, α) of the modified hard-sphere-like approach have similar physical implications. Both approaches clearly demonstrate that the segregation or phase separation in a binary mixture is an outcome of the energetic effect.

It is of interest in particular to visualize the energetics of a binary mixture in terms of pairwise interaction V_{ij} and the radial distribution function $g_{ij}(r)$. Recently, Young [18] showed the equivalence of the lattice based model to that of statistical mechanical approach by noting that the Helmholtz function F can be expressed as

$$F = E - TS, \tag{4.1}$$

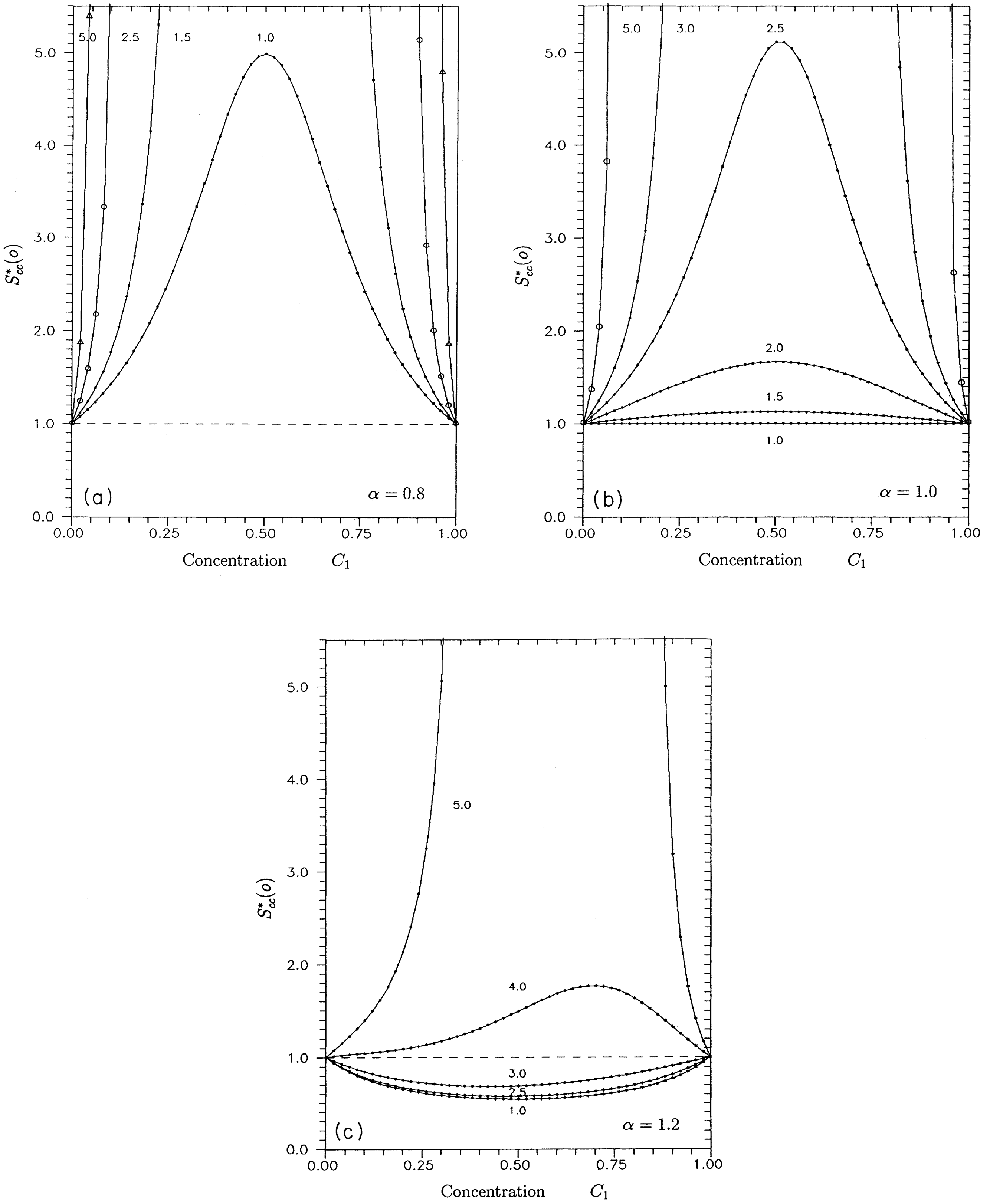

FIG. 4. Reduced $S^*_{cc}(0)$ vs concentration for a binary mixture of size ratio $\gamma = 1.0$ and constant nonadditivity parameter α but with different energy ratio β. (a) $\alpha = 0.8$, $\beta = 1.0$, 1.5, 2.5, and 5.0. (b) $\alpha = 1.0$, $\beta = 1.0$, 1.5, 2.0, 2.5, 3.0, and 5.0. (c) $\alpha = 1.2$, $\beta = 1.0$, 2.5, 3.0, 4.0, and 5.0.

with

$$E = \tfrac{3}{2}k_BT + E_o(\Omega) + \tfrac{1}{2}\rho\sum C_iC_j\int V_{ij}(r)\mathbf{g}_{ij}(r)d\mathbf{r}. \tag{4.2}$$

$E_o(\Omega)$ is the volume dependent term, $\rho(=\Omega^{-1})$ the number density, and S the entropy. Equation (4.2) can readily be expressed as

$$E = \tfrac{3}{2}k_BT + E_0(\Omega) + \tfrac{1}{2}(C_1^2\mathcal{W}_{11} + 2C_1C_2\mathcal{W}_{12} + C_2^2\mathcal{W}_{22}), \tag{4.3}$$

with

$$\mathcal{W}_{ij} = \rho\omega_{ij} \quad \text{and} \quad \omega_{ij} = \int V_{ij}(r)\mathbf{g}_{ij}(r)d\mathbf{r}. \tag{4.4}$$

It is the combination of $\mathcal{W}_{ij}$, which acts as an interchange energy "$\mathcal{W}$" in the quasilattice theory of Sec. I, i.e.,

$$\begin{aligned}\mathcal{W} &= \mathcal{W}_{11} - 2\mathcal{W}_{12} + \mathcal{W}_{22} \\ &= \rho(w_{11} - 2w_{12} + w_{22}) = \rho\omega. \end{aligned} \tag{4.5}$$

By taking ω_{ij} independent of C and the volume, Ω $(= C_1\Omega_1 + C_2\Omega_2)$ linear in C, Young [18] obtained an equation of $S_{cc}(0)$ similar to equation (2.12) $(\gamma_1 = \Omega_1, \gamma_2 = \Omega_2)$.

(b) Both approaches, i.e., QLT and hard sphere, clearly demonstrate that the segregation or phase separation in a binary mixture is an outcome of the energetic effect.

(c) Size effect alone does not yield $S_{cc}(0) > S_{cc}^{\text{id}}(0)$. In the absence of energetic effects, any mismatch size ratio is insufficient to bring segregation in a binary mixture.

(d) The present observation seems to contradict the conclusion that is arrived at with the hard-sphere model in Ref. [9]. We may recall that the divergence in $S_{cc}(0)$ $[S_{cc}(0) \gg S_{cc}^{\text{id}}(0)]$ in the latter work is achieved by optimizing the radial distribution function $g_{ij}(r)$ through a parameter s to the exact virial expansion results. It may be that such an optimation, say, their parameter s, infuses energetic effects into the hard-sphere-like model and, hence, the phase separation results.

More recently, Dijkstra and Frenkel [19] have performed computer simulation studies of a mixture consisting of large and small cubes where the independent variables were the figacities of the cubes. They observed a demixing transition in an additive hard-core lattice mixture. The implications of such results on the usual hard-sphere model remain to be analyzed. However, quite falling in line, the observation of Lekkerkerker and Stroobants [20] regarding the binodal instability in a mixture of hard spheres is interesting. These authors conclude that the origin of the instability is the attractive depletion interaction between the large spheres.

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