Determination of favorable inter-particle interactions for formation of substitutionally ordered solid phases from a binary mixture of oppositely charged colloidal suspensions

Ganeshprasad Pavaskar and Sudeep N. Punnathanam

Citation: J. Chem. Phys. 138, 174504 (2013); doi: 10.1063/1.4802784
View online: http://dx.doi.org/10.1063/1.4802784
View Table of Contents: http://jcp.aip.org/resource/1/JCPSA6/v138/i17
Published by the American Institute of Physics.

Additional information on J. Chem. Phys.
Journal Homepage: http://jcp.aip.org/
Journal Information: http://jcp.aip.org/about/about_the_journal
Top downloads: http://jcp.aip.org/features/most_downloaded
Information for Authors: http://jcp.aip.org/authors

ADVERTISEMENT

Goodfellow
metals • ceramics • polymers • composites
70,000 products
450 different materials
small quantities fast

www.goodfellowusa.com
Determination of favorable inter-particle interactions for formation of substitutionally ordered solid phases from a binary mixture of oppositely charged colloidal suspensions

Ganeshprasad Pavaskar and Sudeep N. Punnathanam

Department of Chemical Engineering, Indian Institute of Science, Bangalore, Karnataka 560012, India

(Received 23 January 2013; accepted 10 April 2013; published online 1 May 2013)

The solid phase formed by a binary mixture of oppositely charged colloidal particles can be either substitutionally ordered or substitutionally disordered depending on the nature and strength of interactions among the particles. In this work, we use Monte Carlo molecular simulations along with the Gibbs-Duhem integration technique to map out the favorable inter-particle interactions for the formation of substitutionally ordered crystalline phases from a fluid phase. The inter-particle interactions are modeled using the hard core Yukawa potential but the method can be easily extended to other systems of interest. The study obtains a map of interactions depicting regions indicating the type of the crystalline aggregate that forms upon phase transition. © 2013 AIP Publishing LLC.

I. INTRODUCTION

Colloidal suspensions consisting of a mixture of oppositely charged particles have been shown to self-assemble into crystalline substitutionally ordered solid phases. Materials made from such substitutionally ordered crystalline aggregates find potential applications in many technologies such as photonics, catalysis, sensing, plasmonics, etc. They display novel chemical or physical properties that are different from those of individual particles. These properties can be tuned through a suitable selection of materials for each type of particle and also through variation in the properties of individual particles such as their size, shape, etc.

For a given set of colloidal particles, the structures of the crystalline aggregates strongly depend on factors such as composition of the fluid phase, charge screening, and charge asymmetry. This dependence has been exploited by many researchers to synthesize crystalline aggregates of various structures. Bartlett and Campbell and Leunissen et al. have synthesized three-dimensional superlattices from a binary mixture of equal-sized but oppositely charged colloids through self-assembly. In both these studies, the magnitude and the sign of the charges on the particles were manipulated through variation of salt concentration in the solvent medium. The salt concentration also affects the magnitude of the Debye screening length. Weakly charged particles at high volume fractions self-assembled into a random hexagonal close packed (rhcp) structure. However, by suitably fine tuning the inter-particle interactions, both groups were able to synthesize superlattices with structures analogous to CsCl and NaCl crystals. Leunissen et al. also successfully synthesized superlattices from unequal-sized colloidal particles. Self-assembly of binary mixtures consisting of metallic and semi-conductor particles with sizes in the nanometer regime were performed by Shevchenko et al. and Kalsin et al. In these studies too, self-assembly of superlattices were achieved only after suitably fine-tuning the inter-particle interactions such as charge screening and charge asymmetry. The synthesis of superlattices through self-assembly would be greatly assisted by a map of interactions depicting regions of stability of various crystal structures.

From a theoretical standpoint, the formation of crystalline aggregates from colloidal suspensions is equivalent to a first-order fluid to solid phase transition. This enables application of techniques to compute phase equilibria towards study of formation of these crystalline aggregates. In a recent work by Pavaskar, Sharma, and Punnathanam, the solid-fluid phase diagrams of a binary mixture of equal sized and oppositely charged colloidal particles were computed using Monte Carlo molecular simulations. The particle interactions were modeled using the hard-core Yukawa potential. Under the conditions studied, the system showed two types of solid phases: a substitutionally ordered crystalline phase having a body-centered cubic structure analogous to CsCl and a substitutionally disordered face-centered cubic (FCC) structure. In general, the CsCl phase was favored when the fluid consisted of equimolar or close to equimolar amounts of oppositely charged particles whereas the FCC phase was favored when one of the components exceeded the other by a large amount. At an intermediate fluid composition, there exists a triple point where the fluid, CsCl, and FCC phases are in equilibrium. For a particular temperature or pressure, the location of the triple points gives the composition range for the formation of the substitutionally ordered CsCl phase from a fluid. The location of the triple point is affected by various factors such as temperature, charge asymmetry, and charge screening. The study by Pavaskar, Sharma, and Punnathanam revealed that the composition range is highest when the magnitude of the charges are equal and decreases sharply with the introduction of charge asymmetry. For highly charge asymmetric mixtures, the phase transition only gives substitutionally

---

a)Author to whom correspondence should be addressed. Electronic mail: sudeep@chemeng.iisc.ernet.in

---
disordered FCC phase. The study\textsuperscript{14} also revealed the existence of an optimum range of charge screening that favored the formation of CsCl phase.

The pressure-composition phase diagrams computed by Pavaskar, Sharma, and Punnathanam\textsuperscript{14} was at a single temperature and for specific values of charge screening and charge asymmetry. In this article, we extend those calculations of solid-fluid phase equilibria to determine the range of conditions that favor the formation of substitutionally ordered crystalline phases such as CsCl phase. We specifically determine the triple point between the CsCl phase, the FCC phase, and the fluid phase with equimolar composition. The triple point represents the boundary between conditions that favor CsCl versus those that favor FCC phase. The variation of the triple point is then computed across various value of charge screening, charge asymmetry, and temperature using Kofke’s method of Gibbs-Duhem integration.\textsuperscript{15, 16} The final result is a map of interactions depicting regions indicating the presence of an optimum range of charge screening that favored CsCl versus those that favor FCC phase. The variation of the triple point between the CsCl phase, the FCC phase, and the fluid is in equilibrium with the CsCl phase. However, within the conditions studied, either the fluid is in equilibrium with FCC phase and at lower values the fluid is in equilibrium with the CsCl phase. The location of the triple point depends on the value of $T^*$, $\kappa\sigma$, and $\alpha$. Our aim is to trace the locus of triple points as a function of $T^*$, $\kappa\sigma$, and $\alpha$. Using Kofke’s method of Gibbs-Duhem integration.\textsuperscript{15, 16} The derivations of the differential equations required for the Gibbs-Duhem integration are as follows.

\textbf{A. Variation of chemical potential and molar Gibbs free energy}

The chemical potential, $\mu$ of a component in the fluid or FCC phase is a function of temperature, pressure, composition, charge ratio, and charge screening, i.e.,

$$d\beta\mu_A = \left(\frac{\partial \beta\mu_A}{\partial T}\right)_{P,\kappa\sigma,\alpha,x_A} dT + \left(\frac{\partial \beta\mu_A}{\partial P}\right)_{T,\kappa\sigma,\alpha,x_A} dP$$

$$+ \left(\frac{\partial \beta\mu_A}{\partial \kappa\sigma}\right)_{T,P,\alpha,x_A} d\kappa\sigma$$

$$+ \left(\frac{\partial \beta\mu_A}{\partial \alpha}\right)_{T,P,\kappa\sigma,x_A} d\alpha + \left(\frac{\partial \beta\mu_A}{\partial x_A}\right)_{T,P,\kappa\sigma,\alpha} dx_A,$$

(2)

$$d\beta\mu_B = \left(\frac{\partial \beta\mu_B}{\partial T}\right)_{P,\kappa\sigma,\alpha,x_A} dT + \left(\frac{\partial \beta\mu_B}{\partial P}\right)_{T,\kappa\sigma,\alpha,x_A} dP$$

$$+ \left(\frac{\partial \beta\mu_B}{\partial \kappa\sigma}\right)_{T,P,\alpha,x_A} d\kappa\sigma$$

$$+ \left(\frac{\partial \beta\mu_B}{\partial \alpha}\right)_{T,P,\kappa\sigma,x_A} d\alpha + \left(\frac{\partial \beta\mu_B}{\partial x_A}\right)_{T,P,\kappa\sigma,\alpha} dx_A,$$

(3)

where $\beta = 1/k_BT$, $P$ is the pressure, and $x_A$ is the mole fraction of component A. For a binary system, the chemical potentials can be written in terms of the molar Gibbs free energy, $G$, as

$$\mu_A = G + (1 - x_A) \left(\frac{\partial G}{\partial x_A}\right)_{T,P,\kappa\sigma,\alpha},$$

$$\mu_B = G - x_A \left(\frac{\partial G}{\partial x_A}\right)_{T,P,\kappa\sigma,\alpha}.$$

Substitution of these identities in the Eqs. (2) and (3) followed by application of thermodynamic relations results in the following equations:

$$d\beta\mu_A = \beta H_A d\beta + \beta V_A d\beta + \beta W_A d\kappa\sigma + \beta T_A d\alpha$$

$$+ (1 - x_A) \left(\frac{\partial \Delta\mu}{\partial x_A}\right)_{T,P,\kappa\sigma,\alpha} dx_A,$$

(4)

III. GIBBS-DUHEM INTEGRATION

For a system of oppositely charged particles, the properties that can be easily tuned are charges on particles and the extent of electrostatic screening. This is equivalent to variation of the reduced variables $T^* (= k_BT/\epsilon)$, $\kappa\sigma$, and $\alpha$, where $T$ is the temperature and $k_B$ is the Boltzmann constant. In Ref. 14, it was observed that for $T^* = 1.0$ and $\alpha = -1$, the equimolar fluid crystallized into the CsCl phase when $\kappa\sigma = 6.0$ and into FCC phase when $\kappa\sigma \to \infty$. Hence at a definite value of $\kappa\sigma > 6.0$, all the three phases will be in equilibrium. When $\kappa\sigma$ is larger than this particular value, the fluid is in equilibrium with FCC phase and at lower values the fluid is in equilibrium with the CsCl phase. The location of the triple point depends on the value of $T^*$, $\kappa\sigma$, and $\alpha$. Our aim is to trace the locus of triple points as a function of $T^*$, $\kappa\sigma$, and $\alpha$ using Kofke’s method of Gibbs-Duhem integration.\textsuperscript{15, 16} The derivations of the differential equations required for the Gibbs-Duhem integration are as follows.
\[ \frac{d \beta}{H_B} + \beta V_B dP + \beta W_B d\kappa + \beta Y_B d\alpha = 0, \]
\[ -x_A \left( \frac{\partial \Delta \mu}{\partial x_A} \right)_{T, P, \kappa, \sigma} \]
\[ \text{where } H \text{ is the molar enthalpy, } V \text{ is the molar volume, } W = (\partial G/\partial \kappa)_{T, P, \sigma, x, } Y = (\partial G/\partial \alpha)_{T, P, \kappa, x, s, } \text{ and } \Delta \mu = \mu_A - \mu_B. \] In these equations, the overline indicates partial molar property of a component.

The substitutionally ordered CsCl phase has an invariant composition. Similar to the above derivation, the variation of the molar Gibbs free energy for the CsCl phase is obtained as
\[ d \beta G = H d\beta + \beta V dP + \beta W d\kappa + \beta Y d\alpha. \]

**B. Two-phase equilibrium**

The criteria for phase equilibrium between the fluid phase and FCC phase are
\[ \mu_A^{(l)} = \mu_A^{(s)}, \]
\[ \mu_B^{(l)} = \mu_B^{(s)}, \]
where the superscripts \( l \) and \( s \) represent the fluid phase and the FCC phase, respectively. If the fluid composition is kept fixed then, upon substitution from Eqs. (4) and (5) followed by elimination of \( x_A^l \) we have
\[ H^{(l-s)} d\beta + \beta V^{(l-s)} dP + \beta W^{(l-s)} d\kappa + \beta Y^{(l-s)} d\alpha = 0, \]
\[ \text{where } H^{(l-s)} = x_A^{(s)} (H_A^{(l)} - H_A^{(s)}) + x_B^{(s)} (H_B^{(l)} - H_B^{(s)}), \]
\[ V^{(l-s)} = x_A^{(s)} (V_A^{(l)} - V_A^{(s)}) + x_B^{(s)} (V_B^{(l)} - V_B^{(s)}) \]
\[ W^{(l-s)} = x_A^{(s)} (W_A^{(l)} - W_A^{(s)}) + x_B^{(s)} (W_B^{(l)} - W_B^{(s)}) \]
\[ Y^{(l-s)} = x_A^{(s)} (Y_A^{(l)} - Y_A^{(s)}) + x_B^{(s)} (Y_B^{(l)} - Y_B^{(s)}). \]

The criteria for equilibrium between the fluid phase and the CsCl phase is given as
\[ G^{(c)} = \frac{\mu_A^{(l)} + \mu_B^{(l)}}{2}, \]
where the superscript \( c \) represents the CsCl phase. Again keeping the fluid composition fixed, upon substitution from Eqs. (4)-(6) we have
\[ H^{(l-c)} d\beta + \beta V^{(l-c)} dP + \beta W^{(l-c)} d\kappa + \beta Y^{(l-c)} d\alpha = 0, \]

\[ \text{where } H^{(l-c)} = (H^{(l)} - H^{(c)}), \]
\[ V^{(l-c)} = (V^{(l)} - V^{(c)}), \]
\[ W^{(l-c)} = (W^{(l)} - W^{(c)}), \]
\[ Y^{(l-c)} = (Y^{(l)} - Y^{(c)}). \]

**C. Three-phase equilibrium**

Equations (7) and (8) give the loci of points corresponding to the fluid-FCC phase equilibrium and fluid-CsCl phase equilibrium, respectively. The degree of freedom for the two-phase equilibrium is three. The intersection of these loci gives the three phase equilibrium between the fluid, FCC, and CsCl phase with the degree of freedom equal to two. The equations determining the three-phase equilibrium are as follows.

Eliminating \( T \) from Eqs. (7) and (8) we get
\[ \left( V^{(l-s)} H^{(l-c)} - V^{(l-c)} H^{(l-s)} \right) dP + \left( W^{(l-s)} H^{(l-c)} - W^{(l-c)} H^{(l-s)} \right) d\kappa \sigma + \left( Y^{(l-s)} H^{(l-c)} - Y^{(l-c)} H^{(l-s)} \right) d\alpha = 0. \]

Eliminating \( P \) from Eqs. (7) and (8) we get
\[ \left( H^{(l-s)} V^{(l-c)} - H^{(l-c)} V^{(l-s)} \right) d\beta + \beta (W^{(l-s)} V^{(l-c)} - W^{(l-c)} V^{(l-s)}) d\kappa \sigma + \beta (Y^{(l-s)} V^{(l-c)} - Y^{(l-c)} V^{(l-s)}) d\alpha = 0. \]

Eliminating \( \kappa \sigma \) from Eqs. (7) and (8) we get
\[ \left( H^{(l-s)} W^{(l-c)} - H^{(l-c)} W^{(l-s)} \right) d\beta + \beta (V^{(l-s)} W^{(l-c)} - V^{(l-c)} W^{(l-s)}) dP + \beta (Y^{(l-s)} W^{(l-c)} - Y^{(l-c)} W^{(l-s)}) d\alpha = 0. \]

Eliminating \( \alpha \) from Eqs. (7) and (8) we get
\[ \left( H^{(l-s)} Y^{(l-c)} - H^{(l-c)} Y^{(l-s)} \right) d\beta + \beta (V^{(l-s)} Y^{(l-c)} - V^{(l-c)} Y^{(l-s)}) dP + \beta (W^{(l-s)} Y^{(l-c)} - W^{(l-c)} Y^{(l-s)}) d\kappa \sigma = 0. \]

**D. Computation of properties**

The equations derived for the Gibbs-Duhem integration are first order differential equations. The quantities on the right hand side of the differential equation are computed using simulations. These simulations for the fluid phase and substitutionally disordered FCC phase are carried out in the isothermal-isobaric semi-grand ensemble (constant \( N, P, T, \Delta \mu \)) and those for substitutionally ordered CsCl phase were done in the isothermal-isobaric ensemble (constant \( N, P, T \)). The quantities that need to be calculated during Gibbs-Duhem integration include \( H, V, W, \) and \( Y \). These are calculated as
follows:

\[ H = \langle U \rangle + P \langle V \rangle, \]
\[ W = \left( \frac{\partial U}{\partial \kappa \sigma} \right), \]
\[ Y = \left( \frac{\partial U}{\partial \alpha} \right), \]

where \( U \) is the potential energy of the system. In addition, the computation of the partial molar properties in the fluid and FCC phases requires computation of the derivatives of \( H, V, W, \) and \( Y \). These are easily computed in the semi-grand ensemble using the fluctuation theory as follows:

\[ \left( \frac{\partial H}{\partial x_A} \right)_T \approx \frac{\langle H x_A \rangle - \langle H \rangle \langle x_A \rangle}{\langle x_A \rangle^2}. \] (13)

Similar equations can be used to compute partial derivatives for \( V, W, \) and \( Y \) with respect to \( x_A \).

**IV. RESULTS AND DISCUSSION**

The application of the Gibbs-Duhem method requires an *a priori* calculation of one coexistence point. In this study, the starting point for the Gibbs-Duhem integration is the fluid-FCC and fluid-CsCl coexistence point. The composition of fluid phase is \( x_A = 0.5 \). The equilibrium is computed for conditions \( T^* = 1.0, \alpha = -1.0, \) and \( \kappa \sigma = 3.0 \). The method for computation of the phase equilibrium is similar to that described in Ref. 14. The Monte Carlo simulations in the isothermal-isobaric semi-grand ensemble consisted of particle displacements, isotropic volume changes, and identity change moves. The Monte Carlo simulations of the CsCl phase consisted of particle displacements, volume moves, and swap moves between unlike particle. Each of these simulations consisted of 50,000 equilibration cycles and 200,000 production cycles. Unlike the earlier work, the addition of particle swap moves introduces an extra rigor where imperfections in substitutional order of the CsCl phase are allowed. These imperfections become significant at higher temperatures and contribute to the free energy of the CsCl phase. The free energies and the chemical potentials at the reference state are computed using the method of Hamiltonian integration for the fluid phase and Frenkel-Ladd technique for the solid phases. The reference states were \( T^* = 1.0, x_A = 1.0, \) and packing fraction \( \eta = 0.458 \) for the fluid phase; and \( T^* = 1.0, x_A = 1.0, \) and \( \eta = 0.539 \) for the FCC phase. The value of the spring constant used in the Frenkel-Ladd simulations was equal to 650. Since we allowed for particle swap moves in the CsCl phase, the Frenkel-Ladd technique was carried out at a lower temperature of \( T^* = 0.5 \) and \( \eta = 0.539 \) where the acceptance of the particle swap moves was zero. The value of the spring constant used in the Frenkel-Ladd simulations for the CsCl phase was equal to 650.

The coexistence pressures, \( P^* (= P \sigma^3 / \epsilon) \), for the fluid-FCC and fluid-CsCl equilibrium were computed to be equal to \( 11.32 \pm 0.025 \) and \( 11.74 \pm 0.03 \), respectively. As mentioned earlier, these serve as the starting point for the Gibbs-Duhem integration. The triple point is computed by integrating Eqs. (7) and (8) at constant \( T^* = 1.0 \) and \( \alpha = -1.0 \). All

FIG. 1. Variation of coexistence pressure at the fluid-FCC and fluid-CsCl phase equilibrium at constant \( T^* = 1.0 \) and \( \alpha = -1.0 \).

The values of \( P^* \) and \( \kappa \sigma \) at this triple point are equal to 12.02 ± 0.055 and 19.75 ± 0.517, respectively. The determination of the triple point allows us to study its variation across \( T^*, \kappa \sigma, \) and \( \alpha \) using Eqs. (9)–(12). The variation of the triple point at constant \( T^* = 1.0 \) along the \( \alpha-\kappa \sigma \) plane is shown in Fig. 2. This figure provides a map of inter-particle interactions depicting regions which favor the formation of a particular solid phase. In Fig. 2, the region below the curve represents the conditions (in terms of \( \alpha \) and \( \kappa \sigma \)) at which an equimolar fluid phase upon phase transition forms the CsCl phase while that above the curve represents conditions for the formation of the FCC phase. The curve shows a maximum at \( \kappa \sigma = 6.95 \) where the value of \( \alpha \) is equal to \(-0.71 \). This further validates the conclusion in Ref. 14 that there exists an optimum value of screening, \( \kappa \sigma \), which favors the formation

FIG. 2. The fluid-FCC-CsCl triple point line on the \( \alpha-\kappa \sigma \) plane at \( T^* = 1.0 \) demarcating regions where an equimolar fluid will undergo phase transition to CsCl phase or FCC phase.
of the substitutionally ordered CsCl phase. The existence of this optimum is explained as follows. Since CsCl is substitutionally ordered, it has a lower energy and entropy compared to the FCC phase. When competing with the FCC phase, it is favored if its energy is sufficiently lower than the FCC phase. At high values of $\kappa \sigma$, the energy of interaction among the particles is reduced. This favors the formation of the FCC phase. The gain in the energy due to substitutional order of CsCl also decreases at lower than optimum values of $\kappa \sigma$ but for different reasons. When the extent of charge screening decreases the range of interaction increases. So in the CsCl phase, each particle interacts not only with its oppositely charged nearest neighbors but also similarly charged next nearest neighbors, lowering the gain in the energy of the CsCl phase compared to the FCC phase. This again favors the formation of the FCC phase. During these investigations, the interaction energies in the Monte Carlo simulations were computed using a spherical cutoff equal to $2.5 \sigma$ followed by incorporation of long range interactions assuming uniform concentrations. Since this approximation fails at low values of $\kappa \sigma$, the lower limit of $\kappa \sigma$ was kept equal to 3.0.

We also computed the triple points at various temperatures. Again these were computed by integrating Eqs. (9)–(12). The computed triple points are shown in Fig. 3. The lowest temperature explored was $T^* = 0.5$. Simulations of the fluid phase at $T^* < 0.5$ are difficult since the oppositely charged particles stick to each other and form a gel-like network. The maximum temperature that favors the formation of the CsCl phase was computed to be $T^* = 1.37$. Figure 3 shows that the optimum value of $\kappa \sigma$ that favors the formation of the CsCl phase is nearly invariant with a value close to 7.0 (see Fig. 4). Figure 5 shows the minimum value of $\alpha$ that is necessary for the formation of CsCl phase. Figure 3 thus provides us with a map of inter-particle interactions showing regions that favor the formation of various solid phases. We can compare this map with the conditions under which the CsCl superlattice was synthesized as reported in Ref. 7. In that study, the values of $\alpha$ and $\kappa \sigma$ were equal to $-0.682$ and 7.263, respectively. The contact energy of oppositely charged particles as computed using Eq. (2) of Ref. 7 was equal to $-1.86 k_B T$. The contact energy as obtained from Eq. (1) is $-0.682 \epsilon$. (This value is obtained by setting $Z_A = 1.0$ and $Z_B = \alpha$.) Equating the two values of the contact energy we obtain $T^* = k_B T / \epsilon = 0.367$. This condition under which the CsCl superlattice was synthesized is depicted in Fig. 3 by the cross symbol. For $T^* = 0.367$, this point lies in the region favoring the formation of CsCl phase from an equimolar binary mixture of oppositely charged particles indicating consistency of our simulation results with the experimental data of Leunissen et al.7 Interestingly, the value of $\kappa \sigma$ is close to the optimum value as shown in Fig. 4. The variation of pressure and packing fraction of the fluid phase at coexistence along the triple point lines are shown in Figs. 6 and 7, respectively. Interestingly, the fluid phase packing fraction is nearly constant along the triple point lines.

As mentioned earlier, the simulations of CsCl phase included particle swap moves, which create imperfections in the substitutional order of the particles. These imperfections were quantified using an order parameter, $\theta$, which is defined as the average mole fraction of particle B among the eight nearest neighbors of A particles. For a perfect substitutional order,
value of $\theta$ is equal to one and for complete random mixing the value of $\theta$ will be equal to 0.5. The value of $\theta$ will depend on temperature, packing fraction, $\kappa\sigma$, and $\alpha$. Figure 8 shows the values of $\theta$ at various points along the three-phase equilibrium lines. Remarkably, the value of $\theta$ is nearly independent of $T^*$. These values can be considered as the lower limit of $\theta$ for the CsCl phase. During synthesis of CsCl superlattice via self-assembly, the conditions will usually be far away from the three-phase equilibrium line. Under these conditions, the average potential energy due to attraction between oppositely charged particles will be higher and consequently one should expect a higher value for $\theta$.

Finally we would like to comment on the nature of the triple points computed. In this study, the triple points represent coexistence between the fluid phase at equimolar composition, the FCC phase, and CsCl phase. At this triple point, the composition of the FCC phase is not equimolar in general. The FCC phase is equimolar only when $\alpha = -1$, i.e., when the system is symmetric. The variation of the composition of the FCC phase is given in Fig. 9. We observe that for asymmetric mixtures, i.e., when $\alpha > -1$, the FCC phase is richer in component B, i.e., $x_A < 0.5$. This can be explained through Fig. 10 which is a schematic of a $P$--$x$ phase diagram at the triple point. The schematic has been constructed based on the prior studies of such systems.14 The $P$--$x$ phase diagram shows two triple points. One of the triple points lie when the fluid composition $x_A = 0.5$. Figure 3 shows the locus of these triple points on the $\alpha$--$\kappa\sigma$ plane. The coexisting FCC phase at this triple point is richer in component B. The other triple point exists for a fluid composition $x_A > 0.5$. Fluids with compositions lying between these two triple points are in equilibrium with the CsCl phase. If we further increase the charge ratio, $\alpha$, keeping the value of $\kappa\sigma$ constant, an equimolar binary Yukawa fluid mixture can only form the FCC phase. However, the CsCl phase can still be formed if the fluid is richer in component A. While constructing the schematic, it is assumed that an azeotrope exists between the fluid and the FCC phase. Further it is also assumed that the FCC phase at the second triple point is also richer in component B. These assumptions may not hold for all the triple points shown in Fig. 3 but other observations regarding the structure of the $P$--$x$ phase diagram will still hold.
FIG. 10. Schematic of a $P-x_A$ phase diagram of a binary mixture of oppositely charged hard core Yukawa particles with a triple point at the fluid composition of $x_A = 0.5$.

V. CONCLUSIONS

In this study, we explored the formation of substitutionally ordered crystalline structures from a binary mixture of equal sized but oppositely charged colloidal particles. Using the method of Gibbs-Duhem integration, the phase equilibria were computed at various temperatures, charge ratio, and charge screening. Under the conditions studied, the only substitutionally ordered crystalline structure that is stable is the one analogous to CsCl. The study confirmed the observation from an earlier work about the existence on an optimum range of charge screening that favors the formation of the CsCl phase. Through this study, we are able to generate a map of interactions depicting regions that favor formation of various solid phases by phase transition from a fluid phase. These results are also consistent with previously published data on synthesis of superlattices from oppositely charged colloidal particles. Although the inter-particle interactions were modeled using the hard core Yukawa potential, this method can be readily applied to colloidal systems with different types of interactions. The maps of interactions generated from such studies provide a useful guide for synthesis of crystalline aggregates of colloidal particles.

ACKNOWLEDGMENTS

The financial support for this work has been provided by grants from the Department of Science and Technology, Government of India.