# Stability of *LS* and *LS*<sub>2</sub> crystal structures in binary mixtures of hard and charged spheres

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We study by computer simulations the stability of various crystal structures in a binary mixture of large and small spheres interacting either with a hard sphere or a screened-Coulomb potential. In the case of hard-core systems, we consider structures that have atomic prototypes CrB,  $\gamma$ CuTi,  $\alpha$ IrV, HgBr<sub>2</sub>, AuTe<sub>2</sub>, Ag<sub>2</sub>Se and the Laves phases (MgCu<sub>2</sub>, MgNi<sub>2</sub>, and MgZn<sub>2</sub>) as well as a structure with space group symmetry 74. By utilizing Monte Carlo simulations to calculate Gibbs free energies, we determine composition versus pressure and constant volume phase diagrams for diameter ratios of q=0.74, 0.76, 0.8, 0.82, 0.84, and 0.85 for the small and large spheres. For diameter ratios 0.76  $\leq q \leq 0.84$ , we find the Laves phases to be stable with respect to the other crystal structures that we considered and the fluid mixture. By extrapolating to the thermodynamic limit, we show that the MgZn<sub>2</sub> structure is the most stable one of the Laves structures. We also calculate phase diagrams for equally and oppositely charged spheres for size ratio of 0.73 taking into consideration the Laves phases, while in the case of oppositely charged spheres, Laves phases are found to be metastable with respect to the CsCl and fluid phases. © 2009 American Institute of Physics. [DOI: 10.1063/1.3182724]

# **I. INTRODUCTION**

Hard spheres are interesting model systems due to their extreme simplicity and yet complex behavior that includes freezing into solid phases and glass formation. While the stable solid structure of pure hard spheres is always the facecentered-cubic (fcc) crystal phase<sup>1</sup> with a maximum packing fraction of  $\sim 0.741$ , the number of stable crystal structures is increased enormously when one considers binary mixtures of large and small hard spheres. The first experimental observations of binary crystal structures of hard-sphere-like particles were made by Sanders<sup>2</sup> in natural gem opals. Later, other authors<sup>3–5</sup> observed binary crystals with the large (L) and small (S) spheres arranged in  $LS_2$  (atomic analog AlB<sub>2</sub>) and  $LS_{13}$  (atomic analog NaZn<sub>13</sub>) structure. It has since been shown that both of these structures are stabilized by entropy alone.<sup>6</sup> The AlB<sub>2</sub> structure is stable at diameter ratios 0.42  $\leq q \leq 0.59$  for the small and large spheres and the NaZn<sub>13</sub> structure is stable at  $0.54 \le q \le 0.61$ .<sup>7-</sup>

The space filling of hard spheres has been used as a starting point for various theoretical studies regarding the phase behavior of binary hard-sphere systems<sup>6,8–10</sup> and to explain experimental observations in binary mixtures of colloids with approximately hard interactions.<sup>4,5</sup> At infinite pressures the crystal structure with the highest close packed density will be stable. However, at lower pressures the stability of a structure is determined by the free energy, which for hard spheres reduces to a purely entropic contribution. It is often asserted in such systems that the free volume per par-

ticle is inversely related to the packing fraction of a crystalline structure and that the entropy is proportional to the free volume. While this argument is incomplete, as evidenced by the stability of the NaZn<sub>13</sub> which has a maximum packing fraction of 0.738 which is lower than for pure fcc, it has been used successfully by various authors to determine which candidate crystalline structures to examine using full free energy calculations.<sup>6,8–10</sup>

Recently, we proposed, based on Gibbs free energy calculations, that LS<sub>2</sub> Laves crystal structures with atomic analogs MgCu<sub>2</sub>, MgNi<sub>2</sub>, and MgZn<sub>2</sub> are stable in the range of  $0.76 \le q \le 0.84$ .<sup>11</sup> All three Laves structures have the same maximum packing fraction,  $\eta \approx 0.710$  at  $q \approx 0.816$ . However, more recently, we examined the packing of binary crystal structures in more detail and a number of additional crystal structures have been identified which pack at least as well as the Laves phases for the size ratios in question.<sup>12</sup> These structures were identified through the combined use of a genetic algorithm (GA) and Monte Carlo (MC) simulations.<sup>12</sup> We briefly sketch the method here, but we would like to refer the reader to Ref. 12 for a more detailed description. We used a GA to locate the energy minima of a fictitious "almost" hard-sphere potential for a certain size ratio and stoichiometry and subsequently, we employed the lowest-energy structures as candidate structures for the best-packed crystal structures for binary hard-sphere mixtures. The optimized structure for the fictitious potential generally does not correspond with the best-packed structure for the hard-sphere mixtures at the same size ratio. We therefore replaced the fictitious potential with a true hard-sphere interaction, ex-

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FIG. 1. The Laves phases and CsCl. The large spheres are dark (red) and the small spheres are light (yellow). (a)  $MgCu_2$ , (b)  $MgZn_2$ , (c)  $MgNi_2$ , (d) CsCl, (e) fcc of large spheres, and (f) fcc of small spheres.

panded the unit cell until all overlaps are removed, and then used a MC pressure annealing simulation to compress the resulting structure to the best packing. The fictitious potential was used to avoid convergence problems which emerge when the packing fraction is used as a fitness function for a GA. Since the packing fraction depends only on the volume of the unit cell and not on the basis vectors, a GA encounters severe convergence problems when it is used as the fitness function.

In the size ratio of interest for this paper, namely, sphere diameter ratios between 0.74 and 0.85 the AB structures which packed best have atomic prototypes CrB, CsCl, and  $\gamma$ CuTi, while the AB<sub>2</sub> structures included HgBr<sub>2</sub>, AuTe<sub>2</sub>, Ag<sub>2</sub>Se, and a structure with the space group symmetry 74 with Wyckoff positions e and f occupied, which we call S74.<sup>12</sup> In this paper we use Gibbs free energy calculations to compare the stability of these various new phases, with the Laves structures and present composition versus pressure and constant volume phase diagrams for binary mixtures of hard spheres for size ratios q=0.74, 0.76, 0.8, 0.82, 0.84, and 0.85. The only stable crystal structures we find on this interval are the Laves phases, with a stability range of  $0.76 \le q$  $\leq 0.84$ . Moreover, we find that MgZn<sub>2</sub> is the most stable of the Laves structures in the thermodynamic limit where the number of particles is taken to infinity. The Laves structures are shown in Figs. 1(a)-1(c), and as can be seen, they differ only in the way the hexagonal layers formed by the doublets of large (red) spheres are packed: In the MgCu<sub>2</sub> structure in Fig. 1(a), this packing is AABBCC, in the  $MgZn_2$  structure in Fig. 1(b) AABB, and in the MgNi<sub>2</sub> structure in Fig. 1(c) AABBAACC. These different packings can be compared to the ABC and AB packings of hexagonal planes in fcc and hexagonal-close-packed (hcp) crystals, respectively.

In addition, we present phase diagrams for binary mixtures of charged spheres for size ratio q=0.73, where the particles interact via screened-Coulomb interactions and are either equally or oppositely charged. In this case we only examine the stability of CsCl and the Laves phases. In the equally charged system we find regions of stability for both the Laves phases as well as CsCl, while in the oppositely charged case we find only CsCl. The work on charged colloids is interesting as it connects with the experimental observations of the Laves structures MgCu<sub>2</sub> and MgZn<sub>2</sub> in mixtures of large and small charged colloids<sup>3,13,14</sup> and also with recent work on binary mixtures of oppositely charged nanoparticles.<sup>15</sup>

To calculate the stability of the phases, both for the hardcore interactions and the charged systems, we calculate the Gibbs free energy using MC simulations. Typically, MC free energy calculations consist of two steps: one first calculates the Helmholtz free energy of a crystal at a single density using the Einstein crystal (or Frenkel-Ladd) method and then combines this with a fitted equation of state from, e.g., constant pressure simulations to give the free energy in the whole density range. This approach is followed in this paper. In addition, we use a similar approach to calculate the free energy of a fluid phase for the charged system with screened-Coulomb interactions. The advantage of the MC free energy calculations compared to the theoretical approaches is that the results are more accurate since there are no approximations and the error only comes from the statistical noise and the finite system size. This allows us to determine the free energy differences between the three Laves structures that all have the same maximum packing fraction, and where the applicability of approaches based on free volume arguments can be doubted. Such an approach is followed in the cell theory by Cottin and Monson.<sup>9,16</sup> In this theory, the free volume, i.e., the configurational integral, of each sphere is sampled using MC simulations with the surrounding spheres frozen at their lattice sites. The individual sphere partition functions are then combined to give the total partition function and hence the free energy. While this approach has been shown to give good agreement with MC simulations,<sup>17-19</sup> it can miss subtle free energy differences such as the difference between the Laves phases.

This paper is organized as follows. In Sec. II, we introduce the methods used to calculate the phase diagrams. In Secs. III A and III B we present the phase diagrams for binary mixtures of hard spheres and screened-Coulomb particles, respectively. We end with conclusions in Sec. IV.

## **II. METHODS**

We consider a binary mixture of  $N_L$  large spheres with diameter  $\sigma$  and  $N_S$  small spheres with diameter  $q\sigma$  where q< 1. In the case of binary hard-sphere mixtures, the pair potential in units of  $k_BT$  between two hard spheres is given by 064902-3 Stability of LS and LS<sub>2</sub> crystal structures

$$\frac{u_{ij}^{\text{HS}}(r)}{k_B T} = \begin{cases} 0 & r \ge \frac{1}{2}(\sigma_i + \sigma_j) \\ \infty & r < \frac{1}{2}(\sigma_i + \sigma_j), \end{cases}$$
(1)

with *r* the center of mass difference between spheres *i* and *j* and  $\sigma_i$  the diameter of particle *i*. For the binary mixtures of charged spheres, the pair potential is taken to be the screened-Coulomb interaction and a hard-sphere potential as given by the DLVO theory,<sup>20,21</sup>

$$\frac{u_{ij}^{\rm SC}(r)}{k_B T} = \begin{cases} \Gamma_{ij} \frac{\exp(-\kappa r)}{r/\sigma} & r \ge \frac{1}{2}(\sigma_i + \sigma_j) \\ \infty & r < \frac{1}{2}(\sigma_i + \sigma_j), \end{cases}$$
(2)

with the prefactor

$$\Gamma_{ij} = \frac{Z_i Z_j \exp[\kappa(\sigma_i + \sigma_j)/2]}{(1 + \kappa \sigma_i/2)(1 + \kappa \sigma_j/2)} \frac{\lambda_B}{\sigma},$$
(3)

where  $Z_i$  and  $Z_j$  are the numbers of electron charges e on particle species i and j,  $\lambda_B = e^2 / \epsilon k_B T$  is the Bjerrum length of the solvent with dielectric constant  $\epsilon$ , and  $\kappa$  the inverse Debye screening length.

The phase diagrams are determined using common tangent constructions on Gibbs free energy data. The Gibbs free energy G is given by G=F+PV, where F is the Helmholtz free energy, P the pressure, and V the volume. In the case of the binary hard-sphere fluid and the pure face-centered-cubic (fcc) hard-sphere crystal, the Gibbs free energies G are obtained from the analytical functions given in the literature.<sup>22,23</sup> In order to obtain the Gibbs free energy of the remaining crystalline phases of hard spheres and the fcc and fluid phases of charged spheres, the Helmholtz free energy F was calculated using MC simulations and combined with the equation of state (P versus  $\eta$ ) data. Below we describe this procedure in more detail.

The Helmholtz free energies of the solid phases are calculated with the Frenkel–Ladd method<sup>24,25</sup> using MC simulations in the canonical ensemble where the number of particles N, volume V, and temperature T are fixed. In the Frenkel–Ladd method, one starts from an Einstein crystal where the particles are tied to their ideal lattice positions by harmonic springs. Then, the springs are slowly removed and one recovers the original interactions. The auxiliary potential energy function that includes the harmonic springs is given by

$$U_{\lambda}(\mathbf{r}^{N}) = U(\mathbf{r}^{N}) + k_{B}T\lambda \alpha \sum_{i=1}^{N} (\mathbf{r}_{i} - \mathbf{r}_{0,i})^{2} / \sigma^{2}, \qquad (4)$$

where  $\mathbf{r}_{0,i}$  is the lattice position of particle *i*,  $\alpha$  is a dimensionless spring constant, and  $\lambda \in [0, 1]$  is a coupling parameter. For the hard-sphere system,  $U(\mathbf{r}^N)$  in Eq. (4) is given by a sum of hard-core potentials (1), and for the charged system, by a sum of screened-Coulomb and hard-core interactions (2). At  $\lambda = 0$ , we recover the system of interest with the original interactions, while at  $\lambda = 1$ , once the spring constant  $\alpha$  is chosen large enough, the particles do not "feel" each other and the system reduces to an Einstein crystal with Madelung energy  $U(\mathbf{r}_0^N)$  (the potential energy of a crystal with all par-

ticles at their lattice positions). The Helmholtz free energy is obtained from  $^{24-26}$ 

$$F(N, V, T) = F_{\text{Ein}}^{\text{CM}}(N, V, T, \alpha) + F_{\text{CM}}(N, V, T)$$
$$- \frac{\alpha k_B T}{\sigma^2} \int_0^1 d\lambda \langle \sum_{i=1}^N (\mathbf{r}_i - \mathbf{r}_{0,i})^2 \rangle_{\lambda}^{\text{CM}}, \tag{5}$$

where the ensemble average  $\langle \cdots \rangle_{\lambda}^{\text{CM}}$  is calculated with the Boltzmann factor  $\exp(-U_{\lambda}/k_BT)$  for a crystal with fixed center of mass. In Eq. (5), the free energy of an Einstein crystal with fixed center of mass is given by

$$F_{\rm Ein}^{\rm CM}(N,V,T,\alpha) = U(\mathbf{r}_0^N) + \frac{3(N-1)}{2}k_BT\ln\left(\frac{\alpha\Lambda^2}{\pi\sigma^2}\right),\tag{6}$$

where  $\Lambda$  is the de Broglie wavelength, and the term

$$F_{\rm CM}(N,V,T) = k_B T \ln\left(\frac{\Lambda^3}{V N^{1/2}}\right) \tag{7}$$

corrects for the fixed center of mass. As noted in Ref. 24, it is useful to rewrite the integral in Eq. (5) as

$$\int_{\ln c}^{\ln(\alpha+c)} (\lambda \alpha + c) \langle \sum_{i=1}^{N} (\mathbf{r}_{i} - \mathbf{r}_{0,i})^{2} / \sigma^{2} \rangle_{\lambda}^{CM} d[\ln(\lambda \alpha + c)], \quad (8)$$

where

$$c = \frac{k_B T}{\langle \sum_{i=1}^{N} (\mathbf{r}_i - \mathbf{r}_{0,i})^2 / \sigma^2 \rangle_0^{\text{CM}}}.$$
(9)

The integral in Eq. (8) is evaluated numerically using a Gauss–Legendre quadrature<sup>27</sup> with 10–20 integration points.

The Helmholtz free energy of a binary fluid of charged spheres can be calculated in a similar manner.<sup>24</sup> The main difference is that in this case the reference state is a binary hard-sphere fluid. For the fluid phase, one uses an auxiliary potential energy function,

$$U_{\lambda}(\mathbf{r}^{N}) = U_{\rm HS}(\mathbf{r}^{N}) + \lambda U(\mathbf{r}^{N}), \qquad (10)$$

where  $\lambda \in [0,1]$  is a coupling parameter and  $U(\mathbf{r}^N)$  is the sum of screened-Coulomb interactions. At  $\lambda = 1$ , we recover the charged system of interest, while at  $\lambda = 0$ , the system reduces to a binary hard-sphere fluid. The Helmholtz free energy is given by

$$F(N, V, T) = F_{\rm HS}(N, V, T) + \int_0^1 \langle U(\mathbf{r}^N) \rangle_{\lambda} d\lambda, \qquad (11)$$

where  $F_{\rm HS}$  is the free energy of a binary hard-sphere fluid.<sup>22</sup> Again, the numerical integration in Eq. (11) is performed using a Gauss–Legendre quadrature.<sup>27</sup>

We calculated Gibbs free energies by first calculating the Helmholtz free energy at a reference state with packing fraction  $\eta_r$ , and then we use equation of state (*P* versus  $\eta$ ) data obtained from constant pressure simulations (where the number of particles  $N_L$  and  $N_S$ , pressure *P*, and temperature *T* are constant) to calculate the Gibbs free energy at all densities. We define the packing fraction  $\eta = \zeta N/V$  with

$$\zeta = \frac{\pi}{6}\sigma^3 [(1-x) + xq^3],$$
(12)

where  $x=N_S/(N_L+N_S)$  is the composition and  $N=N_L+N_S$ . Employing the equation of state  $P(\eta')$  for  $\eta' \in [\eta_r, \eta]$ , the Gibbs free energy at  $\eta$  is obtained from

$$\frac{G(\eta)}{Nk_BT} = \frac{F(\eta_r)}{Nk_BT} + \frac{P(\eta)V}{Nk_BT} + \frac{\zeta}{k_BT} \int_{\eta_r}^{\eta} \frac{P(\eta')}{(\eta')^2} d\eta'.$$
(13)

Equation (13) assumes that the reference packing fraction  $\eta_r$  is within the packing fraction range scanned in the constant pressure simulations. In order to evaluate the integral in Eq. (13), the equation of state data were fitted by analytical functions. For the solid phases, the fitting was done using

$$\frac{PV}{Nk_BT} = \sum_{i=-1}^{n} a_i \gamma(\eta)^i, \qquad (14)$$

where  $\gamma(\eta) = \eta_{cp}/\eta - 1$  and  $\eta_{cp}$  is the maximum packing fraction of the solid.<sup>8</sup> The series was typically truncated at n=3 for the hard-sphere solids and at n=6 or 7 for the solids with screened-Coulomb interactions. For the fluid phase, we used either a simple density expansion,

$$\frac{PV}{Nk_BT} = 1 + \sum_{i=1}^{n} a_i \eta^i,$$
(15)

or a Padé approximation,

$$\frac{PV}{Nk_BT} = 1 + \frac{\sum_{i=1}^{m} a_i \eta^i}{1 + \sum_{i=1}^{n} b_i \eta^i}.$$
(16)

Typical values for truncation of the series were n=5-7 for Eq. (15) and m=6-9 and n=2 for the Padé approximation (16). We performed additional Helmholtz free energy calculations to check that the fitting procedure and the subsequent integration in Eq. (13) produce accurate results.

The ensemble averages for the Helmholtz free energy calculations were obtained from MC simulations that consisted of 20 000–100 000 equilibration steps (trials to displace each particle once) and 20 000–200 000 sampling steps. In the constant pressure simulations, we used 200 000 equilibration steps and 400 000 sampling steps.

The solid free energies calculated using the above procedure have a system-size dependence that scales as 1/N.<sup>26</sup> While in many cases this system-size dependence only has an insignificant effect on the phase behavior, it is an important factor in determining the relative stability of solids that have the same packing efficiency and similar structure, and that therefore can be expected to have nearly equal free energies, as is the case for the fcc and hcp solids.<sup>1</sup> Not surprisingly the free energies of the three Laves phases MgCu<sub>2</sub>, MgZn<sub>2</sub>, and MgNi<sub>2</sub> turned out to be very close to each other. In order to remove the system-size dependency, we used the method introduced in Ref. 26 where one performs free energy calculations for increasing N and extrapolates to the N  $\rightarrow \infty$  limit.

### **III. RESULTS**

## A. Binary mixtures of hard spheres

We determine the phase diagrams for size ratios q=0.74, 0.76, 0.80, 0.82, 0.84, and 0.85 by calculating the Gibbs free energy for CrB,  $\gamma$ CuTi,  $\alpha$ IrV, HgBr<sub>2</sub>, AuTe<sub>2</sub>, AgSe<sub>2</sub>, S74, and the Laves phases. We employ analytical expressions<sup>22,23</sup> for the fluid and the fcc phase. Figures 2–7 show the phase diagrams in the composition  $x=N_S/(N_L)$ +N<sub>s</sub>)-reduced pressure  $p = P\sigma^3/k_BT$  plane. The constant pressure representation follows directly from the common tangent constructions and is the most natural one from a theoretical point of view as this representation can be used e.g., in nucleation studies. In order to compare our results with experimental data, we convert the phase diagram to the corresponding  $\eta_S - \eta_L$  representation. In Figs. 8–13 we show the phase diagrams for the corresponding  $\eta_S - \eta_L$  plane. The only stable solid phases we find for this size ratio are the Laves phases and the pure fcc phases. In the phase diagrams, " $fcc_L$ " and " $fcc_S$ " denote the fcc crystals of pure large and pure small spheres, respectively. The common features in all the phase diagrams are the stable fluid phase at low pressure, a phase coexistence between a fcc crystal of large spheres and the fluid ("fcc<sub>L</sub>+fluid") at elevated pressure for  $x \leq 2/3$ , and a phase coexistence between a fcc crystal of small spheres and the fluid ("fluid+fcc<sub>s</sub>") at elevated pressure and x > 2/3. At very high pressure, we find a coexistence between fcc crystals of pure large and pure small spheres ("fcc<sub>L</sub>+fcc<sub>S</sub>"). From Figs. 3-6 we see that the Laves phases are stable at size ratios  $0.76 \le q \le 0.84$  in the intermediate pressure range between the fcc-fluid coexistence region and the fcc-fcc coexistence. The stable regions of Laves phases consist of a small pocket where the Laves phases coexist with a fluid phase at low pressure followed by larger coexistence regions of fcc and Laves phases at higher pressure. Figures 3-6 show that the Laves phases become stable at p



FIG. 2. Phase diagram of binary hard-sphere mixtures in the composition  $x=N_S/(N_L+N_S)$ -reduced pressure  $p=P\sigma^3/k_BT$  plane with size ratio q =0.74. Labels "fcc<sub>L</sub>+fluid" and "fluid+fcc<sub>S</sub>" denote coexistence regions between a fcc crystal of large (1) or small (s) spheres and a fluid and "fcc<sub>L</sub>+fcc<sub>S</sub>" denotes a coexistence region between fcc crystals of large and small spheres.



FIG. 3. Phase diagram of binary hard-sphere mixtures in the composition  $x=N_S/(N_L+N_S)$ -reduced pressure  $p=P\sigma^3/k_BT$  plane with size ratio q =0.76. The labels are the same as in Fig. 2, and additionally "fcc<sub>L</sub>+Laves," "Laves+fcc<sub>S</sub>," and "Laves+fluid" denote the coexistence regions between the Laves phase and a fcc crystal of large (1) or small (s) spheres or a fluid.

 $\approx 25$  for all size ratios  $0.76 \le q \le 0.84$ . We also see that when q increases from 0.82 to 0.84, the region of stable Laves phases first shrinks and then disappears at q=0.85. Similar behavior is observed at lower size ratios when q decreases from 0.8 to 0.76 and 0.74.

Figure 14 plots the excess Helmholtz free energy per particle  $F_{ex}/Nk_BT$  plus  $\ln(N)/N$  as a function of 1/N at q=0.82 and  $\eta$ =0.6 for the Laves phases MgCu<sub>2</sub>, MgNi<sub>2</sub>, and MgZn<sub>2</sub>. The Helmholtz free energy calculations were performed in a cubic or nearly cubic box. Details of the calculations can be found in Table I. Note that the number of production MC cycles,  $n_{prod}$ , is reduced as the system size is increased without noticeable effect on the accuracy. This can be done because in large systems spatial averaging replaces some of the time averaging. In Fig. 14, the solid lines are linear fits to the data points. As shown in Ref. 26,



FIG. 4. Phase diagram of binary hard-sphere mixtures in the composition  $x=N_S/(N_L+N_S)$ -reduced pressure  $p=P\sigma^3/k_BT$  plane with size ratio q=0.8. The labels are the same as in Fig. 3.



FIG. 5. Phase diagram of binary hard-sphere mixtures in the composition  $x=N_S/(N_L+N_S)$ -reduced pressure  $p=P\sigma^3/k_BT$  plane with size ratio q =0.82. The labels are the same as in Fig. 3.

 $F_{ex}/Nk_BT$ +ln(N)/N is a linear function of 1/N and the intercept at 1/N=0 gives the excess free energy of the infinite bulk system. Analyzing the intercept values, we find that MgZn<sub>2</sub> has the lowest bulk free energy per particle at 7.436 $k_BT$ , followed by MgNi<sub>2</sub> at 7.438 $k_BT$ , and MgCu<sub>2</sub> at 7.439 $k_BT$ . That is, the free energy difference between the three Laves phases is on the order of  $10^{-3}k_BT$  per particle. Due to the small free energy difference, one expects to observe in experiments a mixture of all three Laves phases similar to the experimental observation of the random-hexagonal-close-packed (rhcp) crystals of pure hard spheres, which can be seen as a mixture of fcc and hcp crystals. It is interesting to note that the Laves phases have been observed in binary silicious opal with a diameter ratio of 0.76,<sup>28</sup> in agreement with our predictions.



FIG. 6. Phase diagram of binary hard-sphere mixtures in the composition  $x=N_S/(N_L+N_S)$ -reduced pressure  $p=P\sigma^3/k_BT$  plane with size ratio q =0.84. The labels are the same as in Fig. 3.



FIG. 7. Phase diagram of binary hard-sphere mixtures in the composition  $x=N_S/(N_L+N_S)$ -reduced pressure  $p=P\sigma^3/k_BT$  plane with size ratio q =0.85. The labels are the same as in Fig. 2.

#### B. Binary mixtures of screened-Coulomb particles

In contrast to binary hard-sphere mixtures, no analytical formula exists for the Gibbs free energy of the fluid mixture, CsCl, the Laves phases, and fcc phases of screened-Coulomb particles. Therefore, the Gibbs free energies of all these phases were calculated numerically using the methods presented in Sec. II. The free energies of the fluid mixture were calculated at compositions x=0, 0.05, 0.12, 0.2, 0.4, 0.6, 0.8, 0.95, and 1.0, and the free energies at the intermediate compositions were obtained by interpolation using a fifth order polynomial.

Figures 15 and 17 show phase diagrams of binary mixtures of screened-Coulomb particles with size ratio q=0.73, inverse Debye screening length  $\kappa\sigma=6$ , and Bjerrum length  $\lambda_B/\sigma=0.0051$ . In Fig. 15, the particles are equally charged



FIG. 8. Phase diagram of binary hard-sphere mixtures in the  $\eta_S - \eta_L$  representation with size ratio q=0.74. The labels are the same as in Fig. 2.



FIG. 9. Phase diagram of binary hard-sphere mixtures in the  $\eta_S - \eta_L$  representation with size ratio q=0.76. The labels are the same as in Fig. 3.

with  $Z_L = Z_S = 50$ , while in Fig. 17, the particles are oppositely charged with  $Z_L = -2Z_S = -70$ . These parameter choices are made such that the absolute value of the large-small coupling parameter is  $|\Gamma_{LS}| \approx 12.76$  in both systems. We note here that the system is always charge neutral due to the presence of small ions (taken into account via the inverse screening length  $\kappa$ ) and so the colloid charges do not have to be chosen stoichiometrically. We note that all pair interactions in the system of Fig. 15 are repulsive and that the large and small spheres attract each other in the system displayed in Fig. 17.

Like the phase diagrams presented for the hard-sphere mixtures in Sec. III A, the low pressure region of the phase diagram in Fig. 15 consists of stable fluid and fcc-fluid co-existence regions. At elevated pressure  $(45 \le p \le 60)$ , a



FIG. 10. Phase diagram of binary hard-sphere mixtures in the  $\eta_S - \eta_L$  representation with size ratio q=0.80. The labels are the same as in Fig. 3.





FIG. 11. Phase diagram of binary hard-sphere mixtures in the  $\eta_S - \eta_L$  representation with size ratio q=0.82. The labels are the same as in Fig. 3.

stable Laves phase appears in three pockets of the coexistence with fcc<sub>L</sub>, CsCl, and fluid phases. At high pressure  $(60 \le p \le 70)$ , we find fcc-CsCl coexistence. Finally, at p = 172 (not shown in the figure), CsCl crystal becomes metastable with respect to the coexistence of fcc crystals of pure large and small spheres. As shown in Fig. 16, the zero temperature enthalpy ( $H=U_M+PV$  where  $U_M$  is the Madelung energy) favors the CsCl structure over the FCC structure over a large range of pressures ( $45 \le p \le 207$ ) explaining why the CsCl structure is stable for this weakly repulsive interaction. The observation of stable Laves phases in a system of screened-Coulomb particles at a size ratio below the size-ratio range where Laves phases are stable for hard-



FIG. 12. Phase diagram of binary hard-sphere mixtures in the  $\eta_S - \eta_L$  representation with size ratio q=0.84. The labels are the same as in Fig. 3.



FIG. 13. Phase diagram of binary hard-sphere mixtures in the  $\eta_S - \eta_L$  representation with size ratio q=0.85. The labels are the same as in Fig. 2.

sphere mixtures is in agreement with experiments on charged colloids where MgCu<sub>2</sub> and MgZn<sub>2</sub> structures were observed at size ratios of 0.59-0.71.<sup>3,13,14</sup>

In the phase diagram of the oppositely charged spheres in Fig. 17, the Laves phases are not stable and the phase diagram is dominated by CsCl-fluid and CsCl-fcc coexistence regions. However, this should not be taken as a general result that applies to all systems with oppositely charged spheres as we expect to see stable Laves phases when the strength of the attraction is lowered and the system becomes more hard-sphere-like. This limit corresponds to the experiments on oppositely charged nanoparticle suspensions where MgZn<sub>2</sub> and MgNi<sub>2</sub> structures have been observed.<sup>15</sup> Additionally, the presence of CsCl is consistent with previous studies of oppositely charged colloidal systems.<sup>29–31</sup> The observation of the stable CsCl structure for both a weakly repulsive and oppositely charged systems likely explains why CsCl has been seen in supposedly "hard" interacting colloidal systems.<sup>32</sup>



FIG. 14. Finite-size scaling of the excess Helmholtz free energy,  $F_{\rm ex}/Nk_BT + \ln(N)/N$  vs 1/N at q=0.82 and  $\eta=0.6$  for the Laves phases MgCu<sub>2</sub>, MgNi<sub>2</sub>, and MgZn<sub>2</sub>. The lines are linear fits to the data points.

TABLE I. System sizes and simulation details used to calculate the excess Helmholtz free energies in Fig. 14 for q=0.82 and  $\eta=0.6$ .  $n_{eq}$  and  $n_{prod}$  are the numbers of MC cycles in the equilibration and production runs, respectively, and the error estimate is given by the standard deviation of four independent runs.

Phase	Ν	$n_{\rm eq} \times 10^3$	$n_{\rm prod} \times 10^3$	$F_{\rm ex}/Nk_BT$	<u>+</u>
MgCu <sub>2</sub>	216	40	800	7.3957	0.0010
MgCu <sub>2</sub>	648	40	300	7.4230	0.0010
MgCu <sub>2</sub>	1080	20	100	7.4286	0.0010
MgCu <sub>2</sub>	2592	20	20	7.4347	0.0010
MgCu <sub>2</sub>	5760	20	20	7.4361	0.0010
MgZn <sub>2</sub>	288	40	800	7.4028	0.0003
MgZn <sub>2</sub>	1080	20	100	7.4257	0.0010
MgZn <sub>2</sub>	2304	20	20	7.4315	0.0010
MgZn <sub>2</sub>	4800	20	20	7.4327	0.0004
MgNi <sub>2</sub>	288	40	800	7.4043	0.0004
MgNi <sub>2</sub>	1440	40	100	7.4304	0.0010
MgNi <sub>2</sub>	2304	20	20	7.4327	0.0020
MgNi <sub>2</sub>	5760	20	20	7.4351	0.0005



FIG. 15. Phase diagram of binary mixtures of equally charged ( $Z_L=Z_S$ =50) screened-Coulomb particles in the composition  $x=N_S/(N_L+N_S)$ -reduced pressure  $p=P\sigma^3/k_BT$  plane with size ratio q=0.73,  $\kappa\sigma$ =6, and  $\lambda_B/\sigma$ =0.0051.



FIG. 16. Enthalpy difference ( $\Delta H$ ) between fcc and CsCl crystal structures for equally charged screened-Coulomb particles with composition *x*=0.5, size ratio *q*=0.73,  $\kappa\sigma$ =6, and  $\lambda_B/\sigma$ =0.0051.



FIG. 17. Phase diagram of binary mixtures of oppositely charged screened-Coulomb particles in the composition  $x=N_S/(N_L+N_S)$ -reduced pressure p $=P\sigma^3/k_BT$  plane with charge ratio  $Z_L=-2Z_S=-70$ , size ratio q=0.73,  $\kappa\sigma$ =6, and  $\lambda_B/\sigma=0.0051$ .

#### **IV. CONCLUSIONS**

We have presented phase diagrams in the composition x versus pressure p and in the  $\eta_S - \eta_L$  representation for binary hard-sphere mixtures of large and small hard spheres for size ratios q=0.74, 0.76, 0.8, 0.82, 0.84, and 0.85. The phase diagrams are based on Gibbs free energy data calculated using thermodynamic integration techniques and constant pressure MC simulations. We showed that the Laves structures, MgCu<sub>2</sub>, MgZn<sub>2</sub>, and MgNi<sub>2</sub>, are stabilized by entropy alone and that they are stable with respect to fluid mixtures, binary CsCl, CrB,  $\gamma$ CuTi,  $\alpha$ IrV, HgBr<sub>2</sub>, AuTe<sub>2</sub>, Ag<sub>2</sub>Se, S74, and single component fcc crystal structures at size-ratio range of  $0.76 \le q \le 0.84$ . By extrapolating our free energy data to the infinite system limit, we showed that the free energy difference between the three Laves phases is small, on the order of  $10^{-3}k_BT$  per particle, and that the MgZn<sub>2</sub> crystal has the lowest free energy followed by MgNi<sub>2</sub> and MgCu<sub>2</sub>.

In addition to the binary hard-sphere mixtures, we calculated the full phase diagram of a binary mixture of charged spheres interacting via screened-Coulomb potentials, where the size ratio was q=0.73 and the spheres were equally charged  $(Z_L = Z_S)$  or oppositely charged such that large ones have double the charge of the small ones  $(Z_L = -2Z_S)$ . For the equally charged spheres, we find stable pockets of the Laves phases, indicating that soft repulsion shifts the stability range of Laves phases to lower size ratios q. The last observation is in agreement with experiments on charged colloids where Laves structures MgCu<sub>2</sub> and MgZn<sub>2</sub> were reported in the size-ratio range of 0.59-0.71.<sup>3,13,14</sup> We also find that soft repulsion greatly favors the CsCl phase over Laves phases, thus making the stable pockets of Laves phases smaller. For the system of oppositely charged spheres, the Laves phases are metastable with respect to CsCl and fluid phases. We expect that the Laves phases are stable for a system of oppositely charged colloids once the strength of the attraction is lowered and the system becomes more hard-sphere-like.

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