

# Ionic microgels as model systems for colloids with an ultrasoft electrosteric repulsion: Structure and thermodynamics

D. Gottwald

*Center for Computational Materials Science and Institut für Theoretische Physik, Technische Universität Wien, Wiedner Hauptstraße 8-10, A-1040 Wien, Austria and Institut für Theoretische Physik II, Heinrich-Heine-Universität Düsseldorf, Universitätsstraße 1, D-40225 Düsseldorf, Germany*

C. N. Likos

*Institut für Theoretische Physik II, Heinrich-Heine-Universität Düsseldorf, Universitätsstraße 1, D-40225 Düsseldorf, Germany*

G. Kahl

*Center for Computational Materials Science and Institut für Theoretische Physik, Technische Universität Wien, Wiedner Hauptstraße 8-10, A-1040 Wien, Austria*

H. Löwen

*Institut für Theoretische Physik II, Heinrich-Heine-Universität Düsseldorf, Universitätsstraße 1, D-40225 Düsseldorf, Germany*

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We present a theoretical analysis of the structural properties and phase behavior of spherical, loosely cross-linked ionic microgels that possess a low monomer concentration. The analysis is based on the recently derived effective interaction potential between such particles [A. R. Denton, *Phys. Rev. E* **67**, 011804 (2003)]. By employing standard tools from the theory of the liquid state, we quantitatively analyze the pair correlations in the fluid and find anomalous behavior above the overlap concentration, similar to the cases of star-branched neutral and charged polymers. We also employ an evolutionary algorithm in order to *predict* the crystalline phases of the system *without* any *a priori* assumptions regarding their symmetry class. A very rich phase diagram is obtained, featuring two reentrant melting transitions and a number of unusual crystal structures. At high densities, both the Hansen–Verlet freezing criterion [J.-P. Hansen and L. Verlet, *Phys. Rev.* **184**, 151 (1969)] and the Lindemann melting criterion [F. A. Lindemann, *Phys. Z.* **11**, 609 (1910)] lose their validity. The topology of the phase diagram is altered when the steric interactions between the polymer segments become strong enough, in which case the lower-density reentrant melting disappears and the region of stability of the fluid is split into two disconnected domains, separated by intervening fcc and bcc regions. © 2005 American Institute of Physics.

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## I. INTRODUCTION

Cross-linked polymer networks have been one of the main themes of research in polymer science for many decades.<sup>1</sup> The literature on the topic of uncharged networks is very rich, a review has been presented in Ref. 2. Closely related to these are networks formed by polyelectrolyte (PE) chains. Initial work on such systems, which are also referred to as *polyelectrolyte gels*, focused on the swelling behavior in the presence of salt.<sup>3,4</sup> Active interest in the swelling of these gels remains to date, due to their ability to absorb large amounts of water and act as superabsorbers or drug delivery systems. Theoretical work on the swelling has been summarized in the review article of Khokhlov *et al.*<sup>5</sup> Computer simulations have also played a very important role in understanding the conformations of charged gels,<sup>6–8</sup> where the role of short-range attractions has also been examined.<sup>9</sup>

Scaling down the size of the above-mentioned *macroscopic* cross-linked gels, one obtains mesoscopically sized particles, synthesized by cross linking of polymers that are known as *microgels*.<sup>10,11</sup> The most common polymer of

which microgels are made is poly(*N*-isopropylacrylamide) (PNIPAM), whereas other polymers such as polyacrylic acid<sup>12</sup> or polystyrene<sup>13</sup> can also be used,<sup>10</sup> and the preparation of novel, starch-based microgels has been recently reported as well.<sup>14</sup> Much in similarity with their macroscopic counterparts, microgels can swell in a good solvent and this property makes them promising as drug delivering agents,<sup>12,15</sup> once they have been designed to swell in the vicinity of target sites.<sup>10</sup> Most of the current industrial interest in microgels focuses primarily on their usage in surface-coating applications, due to their ability to act as rheological regulators. At the same time, microgels are of great interest as model colloidal particles, since they can bridge between hard-sphere particles<sup>16</sup> and soft colloids<sup>17</sup> through suitable modifications of their monomer- and cross-linking densities. Depending on whether they carry a net charge or not, microgels can be distinguished into *ionic* or *neutral*. Depending on the monomer concentration in their volume, they are classified as *uniform* or *core-shell* microgels.

In the recent years, considerable work has been done

regarding the internal conformations and swelling properties of microgels and, in particular, the dependence of the latter on parameters such as temperature, pH, solvent quality, net charge, and salt concentration.<sup>17–22</sup> Less is known, however, about the structural properties and phase behavior of macroscopic solutions of microgel particles. Hellweg *et al.*<sup>23</sup> have found that microgel particles form colloidal crystals akin to those occurring in hard-sphere systems, whereas Gröhn and Antonietti have performed static light-scattering experiments, finding scattering intensities typical of dense, liquid-like colloidal systems.<sup>24</sup> Formation of structured clusters from soft microgels has been reported by Fernández-Nieves *et al.*,<sup>25</sup> whereas Fernández-Barbero and Vincent have focused on the complexation between charged microgels and oppositely charged colloids.<sup>26</sup>

A concept that greatly facilitates the theoretical investigations of the structural and thermodynamic properties of complex fluids (such as microgel solutions) is that of the *effective interaction potential* between suitably chosen coordinates that characterize the macromolecular aggregates as a whole.<sup>27</sup> Proposals for the effective potential between dense, hard spherelike microgels have been put forward recently by Wu *et al.*<sup>28,29</sup> as well as by Berli and Quemada.<sup>30</sup> For the opposite case of loosely cross linked, ionic microgels, an effective potential has been derived by Denton<sup>31</sup> within the formalism of linear-response theory, which allows for an (approximate) tracing-out of the counterion degrees of freedom. In a recent publication,<sup>32</sup> we have applied standard tools from the theory of liquids, combined with a novel, evolutionary algorithm to *predict* stable solid phases, drawing thereby the phase diagram of ionic microgel solutions for some selected parameter values. In this paper, we present an extended account on the thermodynamic *and* structural properties of ionic microgel solutions and the correlations between the two for a wide range of parameters. We also offer a more extensive account of the evolutionary algorithm employed previously<sup>32</sup> and we examine the effect of the steric (self-avoidance) interactions on the topology of the phase diagram. The latter have been ignored in the preceding work.<sup>32</sup> In this way, we establish quantitative limits for the range of physical parameters that can cause a change in the topology of the phase diagram.

The rest of the paper is organized as follows: In Sec. II we present and discuss the effective interaction potential, on which all further investigations are based. The properties of the fluid phase are presented in Sec. III, whereas the evolutionary algorithm employed for finding the optimal crystal phases as well as the properties of the solid phases are shown in Sec. IV. The resulting phase diagram is presented and discussed in Sec. V, and the influence of the steric interactions on it is the subject of Sec. VI. Finally, in Sec. VII we summarize and draw our conclusions. Some technical remarks regarding the volume terms of microgel solutions in comparison with those pertaining to hard, charged colloids are relegated to the Appendix.

## II. EFFECTIVE INTERPARTICLE POTENTIALS

We consider  $N$  charged microgels in the volume  $V$ , with density  $\rho = N/V$ . Every microgel carries charge  $Ze$ , with the

elementary charge  $e$ , where the possible Manning-condensed counterions have been subtracted. Due to electroneutrality, the solution also contains  $N_c = ZN$  monovalent counterions. We limit ourselves to the salt-free case only. The system is assumed to be dissolved in water at room temperature. An effective interaction between the microgel particles can be formally derived by taking a partial trace of the canonical partition function  $\mathcal{Z}$  of the system. This task has been carried out recently by Denton,<sup>31</sup> who showed that the original partition function can also be expressed as a canonical trace over the microgel degrees of freedom only, employing a suitably defined effective Hamiltonian  $\mathcal{H}_{\text{eff}}$ , namely,

$$\mathcal{Z} = \langle \exp(-\beta \mathcal{H}_{\text{eff}}) \rangle_{\text{m}}. \quad (1)$$

In Eq. (1) above, the brackets  $\langle \cdots \rangle$  denote a canonical trace and the subscript indicates that it has to be taken with respect to the coordinates and momenta of the microgel particles *only*. Moreover,  $\beta = (k_B T)^{-1}$ , with the Boltzmann constant  $k_B$  and the absolute temperature  $T$ .

The effective Hamiltonian has been shown to have the form<sup>31</sup>

$$\mathcal{H}_{\text{eff}} = \sum_{i=1}^N \frac{\mathbf{P}_i^2}{2m} + \sum_{i < j} v_{\text{eff}}(|\mathbf{R}_i - \mathbf{R}_j|) + E_0, \quad (2)$$

where  $\mathbf{P}_i$  denotes the momentum and  $\mathbf{R}_i$  the position vector of the center of the  $i$ th microgel, and  $E_0$  is a so-called “volume term” to be defined in Eq. (8) below. Each microgel particle has a diameter  $\sigma$ . The effective potential  $v_{\text{eff}}(r)$  possesses two branches, one valid for separations  $r \leq \sigma$  and one for  $r > \sigma$ . For overlapping particles, it has the form

$$v_{\text{eff}}(r) = \frac{2Z^2 e^2}{\epsilon \sigma} \left[ \frac{6}{5} - 2 \left( \frac{r}{\sigma} \right)^2 + \frac{3}{2} \left( \frac{r}{\sigma} \right)^3 - \frac{1}{5} \left( \frac{r}{\sigma} \right)^5 \right] - \frac{72Z^2 e^2}{\epsilon \kappa^4 \sigma^4 r} v_{\text{ind}}(r) \quad (r \leq \sigma), \quad (3)$$

where  $\epsilon$  is the dielectric constant of the solvent and  $v_{\text{ind}}(r)$  is given by the expression

$$v_{\text{ind}}(r) = \left( 1 - e^{-\kappa r} + \frac{1}{2} \kappa^2 r^2 + \frac{1}{24} \kappa^4 r^4 \right) \left( 1 - \frac{4}{\kappa^2 \sigma^2} \right) + \frac{4}{\kappa \sigma} e^{-\kappa \sigma} \sinh(\kappa r) + \left[ e^{-\kappa \sigma} \sinh(\kappa r) + \kappa^2 \sigma r + \frac{1}{6} \kappa^4 (\sigma^3 r + r \sigma^3) \right] \left( 1 + \frac{4}{\kappa^2 \sigma^2} \right) - \frac{4r}{\sigma} \left( 1 + \frac{1}{2} \kappa^2 \sigma^2 + \frac{1}{30} \kappa^4 \sigma^4 \right) - \frac{8r^3}{3\sigma^3} \left( \frac{\kappa^2 \sigma^2}{4} + \frac{\kappa^4 \sigma^4}{12} \right) - \frac{1}{180} \frac{\kappa^4}{\sigma^2} r^6. \quad (4)$$

On the other hand, for nonoverlapping distances the effective interaction crosses over to a screened electrostatic (Yukawa) potential of the form

$$v_{\text{eff}}(r) = \frac{144Z^2e^2}{\epsilon\kappa^4\sigma^4} \left[ \cosh(\kappa\sigma/2) - \frac{2 \sinh(\kappa\sigma/2)}{\kappa\sigma} \right]^2 \frac{e^{-\kappa r}}{r},$$

( $r > \sigma$ ). (5)

In Eqs. (4) and (5) above,  $\kappa$  is the inverse Debye screening length, which, for monovalent counterions and salt-free solutions is given by the expression

$$\kappa = \sqrt{4\pi Z\rho\lambda_B},$$

(6)

with the Bjerrum length  $\lambda_B$  expressing the distance at which the electrostatic interaction between two elementary charges roughly equals the thermal energy, namely,

$$\lambda_B = \frac{e^2}{\epsilon k_B T},$$

(7)

and having the value  $\lambda_B = 7.14 \text{ \AA}$  for water at room temperature. The Bjerrum length is kept fixed to this value throughout this work.

As a result of the partial trace of the partition function of the original system, two effects show up. On the one hand the pair potential acquires an explicit density dependence through the parameter  $\kappa$ . On the other hand, an extensive volume term  $E_0$  appears in the effective Hamiltonian, which contains contributions from the degrees of freedom of the counterions and reads as

$$E_0 = ZNk_B T \left[ \ln(Z\rho\Lambda^3) - 1 \right] - N \frac{6Z^2e^2}{\epsilon\sigma} \left\{ \frac{1}{5} - \frac{2}{\kappa^2\sigma^2} + \frac{6}{\kappa^3\sigma^3} \left[ 1 - \frac{4}{\kappa^2\sigma^2} + \left( 1 + \frac{4}{\kappa\sigma} + \frac{4}{\kappa^2\sigma^2} \right) e^{-\kappa\sigma} \right] \right\} - ZN \frac{k_B T}{2},$$

(8)

where  $\Lambda$  is the thermal de Broglie wavelength. Though  $E_0$  has no influence on the correlation functions of the macromolecules, it forms an integral part of the thermodynamics of the system, as is clear from Eqs. (1) and (2). In Fig. 1(a) we show some selected plots of the effective potential  $v_{\text{eff}}(r)$ , where it can be seen that this quantity is ultrasoft and bounded. Moreover, both the range and the strength of  $v_{\text{eff}}(r)$  shrink with increasing concentration  $\rho$  of the microgels. On the other hand, as can be seen in Fig. 1(b), an increase of the charge number  $Z$  on the microgels renders the potential more steeply repulsive. The volume term  $E_0/V$  is a convex function of the density  $\rho$ , whereas the one pertaining to hard colloids can be concave.<sup>33</sup> A comparison between the two cases is presented in the Appendix.

### III. PROPERTIES OF THE FLUID PHASE

The two quantities of central interest that describe the pair correlations in the fluid phase in real and reciprocal space are the radial distribution function  $g(r)$  and the structure factor  $S(k)$ , respectively. As is clear from Eqs. (3)–(5), the effective interaction at hand is density dependent. As it has been repeatedly pointed out in the literature,<sup>34–37</sup> special care should be taken when dealing with such effective potentials, since it is crucial to take into account the context in

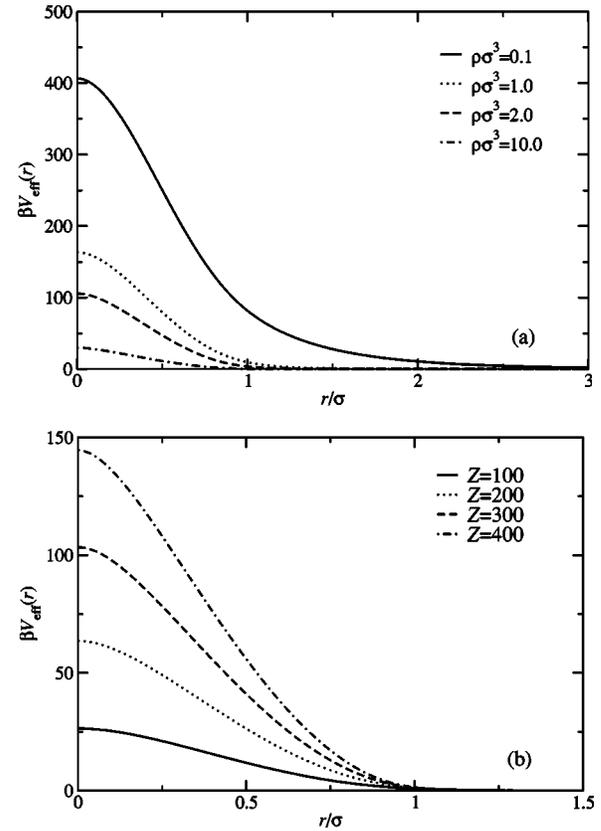


FIG. 1. The effective interaction potential between charged microgels, according to Eqs. (3)–(5). (a) Fixed charge  $Z=200$  and for different microgel densities  $\rho$ ; (b) fixed density  $\rho\sigma^3=1.0$  and varying  $Z$ . The particle diameter has the value  $\sigma=100$  nm.

which they have been derived. In the case at hand, the procedure involved in the derivation of the effective interaction is an approximate tracing out of the counterion degrees of freedom, which has been carried out with the goal of leaving the total free energy of the system unchanged. In other words, the sum of the interaction free energy and the volume terms should be the same as the original free energy of the system. An important consequence of the partial trace over the counterion degrees of freedom, however, is that the compressibility and virial routes to the free energy<sup>38</sup> do not yield identical results.<sup>34</sup> In this sense, neither the “fluctuation compressibility”  $\chi_{\text{fl}}$  given by the  $k \rightarrow 0$  limit of the static structure factor  $S(k)$  nor the “virial compressibility”  $\chi_{\text{vir}}$ , obtained by differentiation of the virial pressure with respect to the density, represent the true compressibility of the system. We can, nevertheless, imagine a putative system with a density-independent interaction potential, which is identical to the present interaction potential  $v_{\text{eff}}(r; \rho_0)$  at a given density  $\rho_0$ . Since at this density the two systems appear identical, they also have the same structure, as given by the functions  $g(r)$  and  $S(k)$ —but *not* the same thermodynamics. Enforcing consistency between the compressibility and virial routes has the additional benefit of improving the agreement between the obtained  $S(k)$  and corresponding simulation results.<sup>39</sup> Hence, we employ the Rogers–Young (RY) closure<sup>40</sup> in order to obtain the correlation functions of the microgel solution at any given density, treating the latter simply as a fixed parameter in the interaction. We reiterate that, although the RY-closure

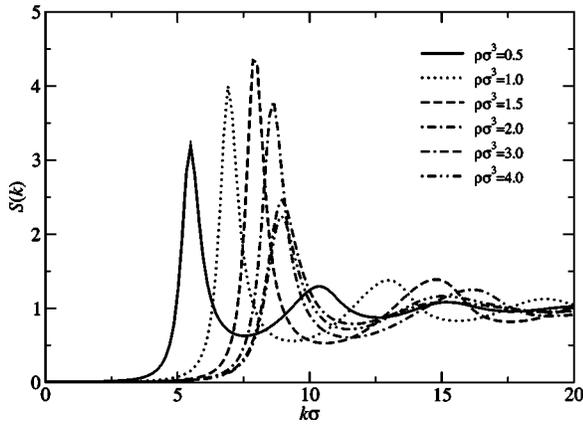


FIG. 2. The structure factor  $S(k)$  for  $Z=250$  and for increasing density  $\rho$ . Note the anomalous behavior of the peak height.

enforces the consistency of the two routes to the compressibility, the resulting quantity does not represent the real compressibility of the system at hand. We have also employed the simpler (and thermodynamically inconsistent) hypernetted chain (HNC) closure to the Ornstein–Zernike relation in order to provide a comparison between the two in obtaining the phase diagrams of Sec. V.

In Fig. 2 we show representative results for the structure factor  $S(k)$  as obtained by the RY closure. We see the characteristic signature of the ultrasoft nature of the interaction, namely, the growth of the height of the main peak of  $S(k)$  up to, roughly, the overlap density  $\rho_*$  of the microgels, which is then followed by an anomalous behavior: on the one hand the height of the main peak starts *decreasing* as the density grows and on the other hand its position changes very weakly with density above  $\rho_*$ . Identical behavior has been seen for solutions of star polymers<sup>39</sup> and polyelectrolyte stars.<sup>41,42</sup> The insensitivity of the location of the peak above the overlap density can be traced back to the crossover of the potential from a Yukawa to a soft interaction and the latter part is only felt above the overlap concentration. The decay of the peak height and the associated loss of correlations at high densities is a result of the ultrasoft character of the interaction and points to a reentrant melting behavior of the system, as it will be shown shortly.

Representative results for the radial distribution function  $g(r)$  are shown in Fig. 3. Here we encounter the unusual behavior that upon increasing the concentration the height of the peak corresponding to the first coordination shell *decreases*. The physical origin of this phenomenon lies in the fact that the interaction potential  $v_{\text{eff}}(r)$  becomes itself softer upon increasing  $\rho$ ; the same behavior has been seen in the case of polyelectrolyte star solutions,<sup>41</sup> where again the interaction is density dependent and softening as  $\rho$  increases, but not in the case of neutral star polymers,<sup>39</sup> where the potential is density independent. Above the overlap density,  $g(r)$  develops an unusual substructure inside the corona diameter  $\sigma$  and the physical reasons behind this behavior have been discussed in detail in Refs. 39 and 41. In view of the striking similarities in the phenomenology of star polymers, polyelectrolyte stars, and ionic microgels, it is fair to say that they all belong to the class of soft matter systems that have

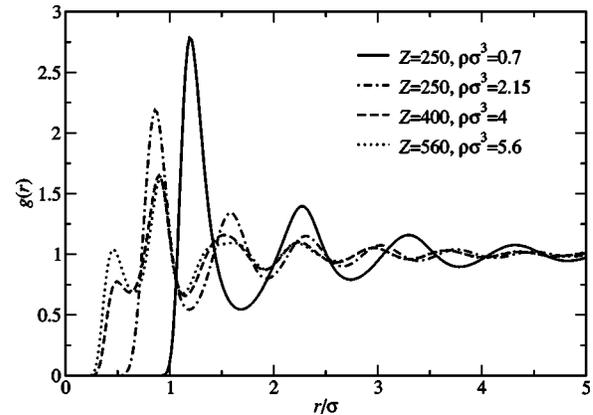


FIG. 3. Radial distribution functions  $g(r)$  for various combinations of  $Z$  and  $\rho$ , as indicated in the legend. The points in the  $(Z, \rho)$  plane have been chosen to lie close to the phase boundaries between the fluid and incipient crystal structures—see Fig. 7.

been termed as *ultrasoft*. Dendritic macromolecules that feature a Gaussian effective potential between their centers of mass are yet another member of this family.<sup>43,44</sup>

The pair correlation functions also offer a way to the thermodynamics of the system via the so-called  $\lambda$ -integration route.<sup>37</sup> Consider the Hamiltonian  $\hat{\mathcal{H}} = \mathcal{H} - E_0$ , with  $\mathcal{H}$  and  $E_0$  being defined in Eq. (2). It can be shown<sup>45</sup> that the excess free energy density  $\hat{f}_{\text{ex}}(\rho)$  associated with  $\hat{\mathcal{H}}$  can be calculated through the relation

$$\beta \hat{f}_{\text{ex}}(\rho) = \frac{1}{2} \rho^2 \int d^3r \beta v_{\text{eff}}(r; \rho) \int_0^1 d\lambda g^{(\lambda)}(r; \rho), \quad (9)$$

where  $g^{(\lambda)}(r; \rho)$  is the radial distribution function corresponding to a fluid interacting by means of the “scaled” potential  $v_{\text{eff}}^{(\lambda)}(r; \rho) = \lambda v_{\text{eff}}(r; \rho)$ . The total free energy density  $f(\rho)$  is then obtained by adding to  $\hat{f}_{\text{ex}}(\rho)$  the ideal and volume-term contributions, namely,<sup>46</sup>

$$\beta f(\rho) = \rho [\ln(\rho \Lambda^3) - 1] + \beta \hat{f}_{\text{ex}}(\rho) + \frac{\beta E_0}{V}. \quad (10)$$

The free energy is shown in Fig. 4 for some characteristic

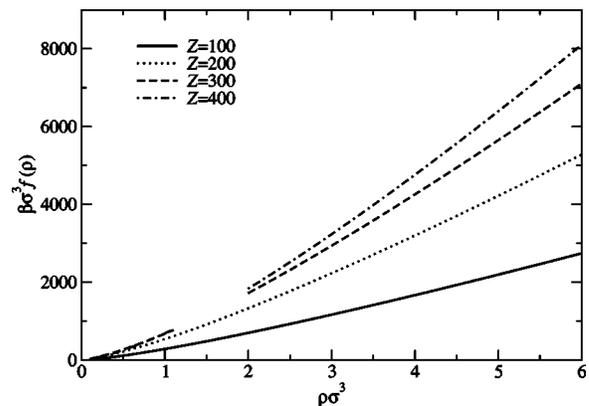


FIG. 4. Free energy density, including the volume term. The density gap represents the region where the solid phases are stable.

values of the charge parameter  $Z$ . Note that the free energy density is free of concave parts, i.e., there is no spontaneous liquid-gas phase separation in the system, in agreement with the fact that the structure factors  $S(k)$  of the microgel particles show no divergence at the limit  $k \rightarrow 0$ . The liquid free energy calculated in the fashion described above has been employed to draw the phase diagrams in Sec. V, in conjunction with the free energies of the solid phases. The way in which these have been calculated is described in the following section.

#### IV. CANDIDATE SOLID PHASES: EVOLUTIONARY ALGORITHM AND HARMONIC THEORY

We now turn to the solid phases: first we have to find out the possible candidate structures into which the ionic microgels can freeze. To this end, we have applied a genetic algorithm (GA) which was recently proposed and implemented by some of us.<sup>47</sup> While up to now equilibrium structures in freezing processes were determined from a preselected set of candidates (an approach which always carried the risk of “forgetting” a possible candidate), our GA is able to predict crystal structures into which the fluid can freeze via an unrestricted, unbiased, and parameter-free search algorithm.

In a more general context, GAs can be considered as optimization strategies that use features of evolutionary processes as key elements; their purpose is to find optimal solutions for a given problem.<sup>48</sup> Originally developed by Holland and co-workers,<sup>49</sup> it has meanwhile been applied in many fields,<sup>48</sup> such as economics, immunology, biology, or computer sciences. Astonishingly enough, the attractive features of GAs have not yet been discovered in physics. In recent work we could demonstrate that GAs can represent also in physics a very powerful tool: they have been used in freezing studies of several systems<sup>47</sup> and have thereby proven to be a reliable, efficient, and accurate tool; we are therefore convinced that in the near future GAs will merit more appreciation in physical problems where their ideas might be applied in a vast variety of problems.

The basic unit in a GA is an individual  $\mathcal{I}$  which, in turn, is built up by a fixed number of genes. In our application an individual contains in a coded form information about a crystal structure; it has been coded by the binary alphabet, i.e., each gene can assume the values 0 or 1 and each individual can be viewed as a binary code of the set of primitive vectors of a Bravais lattice; for nonsimple lattices the positions of the additional particles in the basis unit of the structure (we have restricted the number of basis atoms to eight) have to be included as well. Note that the limited number of genes in an individual leads to a limited accuracy in this representation. Special care has been taken to guarantee that different but equivalent parametrizations of a crystal structure are represented by one individual only; for details we refer again to Ref. 47. Further we assign via a fitness function  $f(\mathcal{I})$  a positive fitness value to each individual  $\mathcal{I}$ ; this is done in the sense that a higher value of this function characterizes a better solution. For the present contribution we have chosen for  $f(\mathcal{I})$  the following form:

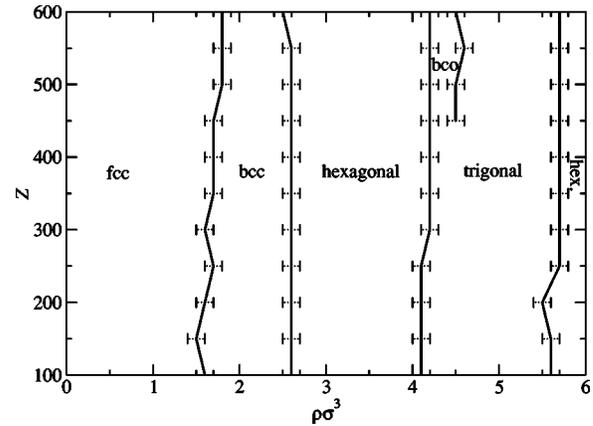


FIG. 5. The ( $T=0$ )-phase diagram of the system, as obtained from the minimization of the lattice sums employing the genetic algorithm.

$$f(\mathcal{I}) = \exp\{-[F(\mathcal{I}) - F(\mathcal{I}_{\text{fcc}})]/F(\mathcal{I}_{\text{fcc}})\}, \quad (11)$$

$F(\mathcal{I})$  is the free energy for a crystal structure represented by the individual  $\mathcal{I}$  and  $\mathcal{I}_{\text{fcc}}$  is the individual representing the fcc lattice. The free energy of any given crystal structure was calculated within a harmonic theory in the approximation of the Einstein model, as we discuss below.

A large number of individuals—in our case 1000—form a generation; the individuals of the first generation are created at random. Triggered by the fitness values of the individuals, pairs of parents are chosen from this generation: they create the individuals of the subsequent, second generation. This is done via a so-called one-point crossover process: cutting both parents at a randomly chosen position, we cross combine the respective parts and create thus two individuals of the second generation. In addition, we perform with a probability  $p_m$ —in our case we chose  $p_m=0.001$ —mutations: in a given generation we flip the value of each gene from 0 to 1 or vice versa with the probability  $p_m$ . In this manner we arrive at a different generation of individuals. We repeat the above steps to create individuals of the subsequent generation and continue this iteration over several steps: our experience has shown that 100 generations are by far sufficient to guarantee convergence.

In each generation we retain the individual with the highest fitness value. Among the “fittest” individuals of each generation, we consider the one with the absolutely highest fitness value to be the best individual, representing thus the solution of the optimization (search) algorithm. Due to the limited accuracy induced by the finite number of genes in an individual (and, consequently, of the binary representation of the lattice parameters) this solution is refined in a subsequent steepest descent minimization, and represents then the stable crystal structure of the search.

The possible candidate structures into which our ionic microgels can freeze have been selected at  $T=0$ , i.e.,  $F=U$ , where for a given crystal structure the internal energy  $U$  has been calculated via a lattice sum. The ( $T=0$ )-phase diagram is depicted in Fig. 5, indicating which crystal structure represents for a given state of the system the stable one. At low densities (i.e., up to  $\rho\sigma^3 \sim 2.5$ ) we encounter for all  $Z$  values the usual suspects, i.e., the fcc and bcc lattices. As we in-

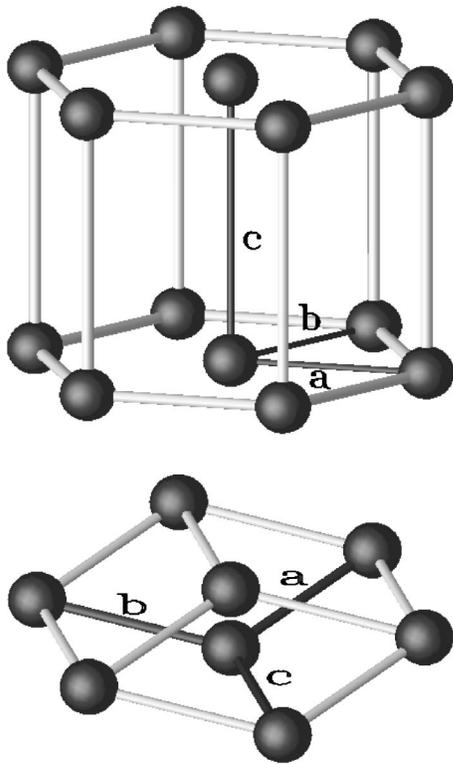


FIG. 6. Representative sections of the hexagonal (top) and the trigonal (bottom) lattices, with the respective elementary unit vectors indicated.

crease the density, interestingly enough—and characteristic for systems with soft potentials—more open structures appear: hexagonal, trigonal with a bco section for higher charges, and hexagonal again. Note that in the phase diagram for star polymers<sup>50</sup> the bco and the diamond structures are encountered, while in polyelectrolyte star solutions the bco, the hexagonal, and the sc structures are the stable crystals.<sup>41</sup> Within the error bars indicated in Fig. 5, the GA is converging to two solutions with equal fitness values, indicating the phase transition from one structure to the other. In Fig. 6 we show representative sections of the hexagonal and the trigonal lattice, along with the respective conventional unit cells.

These five crystal structures define the set of possible candidate structures for the phase diagram; we do not assume that for  $T > 0$  new candidates might emerge in the freezing transition. These phase diagrams are now calculated as already described in Ref. 41: for the five candidate structures we calculate the free energy within the approximate Einstein model<sup>51,52</sup> (for details we refer the reader to Sec. IV of Ref. 41) and compare them with the free energies of the competing fluid phase (see preceding section). They are discussed in the subsequent section.

## V. PHASE BEHAVIOR

In Fig. 7 we show the phase diagram in the  $(Z, \rho\sigma^3)$  plane of our model ionic microgel for  $\sigma = 100$  nm. The parameter  $Z$  represents the bare charge number of the microgel that can be measured at vanishingly small particle concentrations. The net charge number  $Z_{\text{net}}$ , after taking into account

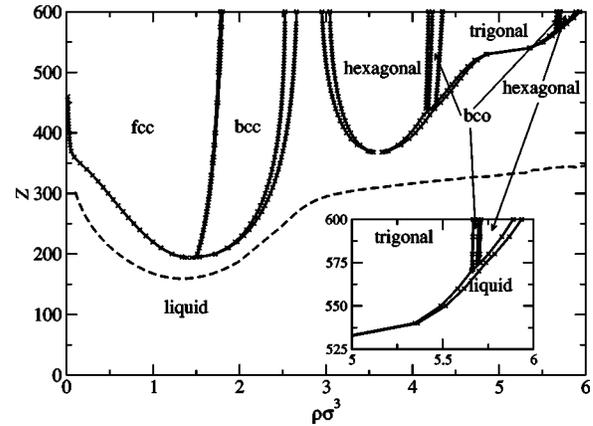


FIG. 7. The phase diagram of ionic microgels, as obtained by the procedure described in the text. The free energy of the fluid has been calculated by employing the RY closure. The dashed line denotes the locus of points on which the main peak of  $S(k)$  attains the Hansen–Verlet value. Here the diameter of the microgels is kept fixed at  $\sigma = 100$  nm.

the counterions absorbed within the microgel is a density-dependent quantity that can be calculated using Eq. (38) of Ref. 31, namely,

$$Z_{\text{net}} = Z \frac{6}{\kappa\sigma} \left( 1 + \frac{2}{\kappa\sigma} \right) e^{-\kappa\sigma/2} \left[ \cosh(\kappa\sigma/2) - \frac{\sinh(\kappa\sigma/2)}{\kappa\sigma/2} \right]. \quad (12)$$

The length scale  $\sigma$  stems from the diameter of the microgel particles at infinite dilution. The microgel size can change at finite concentrations as a result of two competing mechanisms: the increase of the fraction of absorbed counterions, which tend to swell the network, and the osmotic pressure from neighboring microgel particles that lead to shrinkage of the same. Within our theory we are not able to make quantitative predictions as to the density dependence of the particle size. Therefore we scale the density with the unperturbed microgel diameter  $\sigma$ . Steric contributions to the interaction are neglected for the moment; their influence on the phase behavior will be discussed in more detail in Sec. VI. The results are based on the RY closure for the fluid phase. It is easy to check that our potential belongs to the  $Q^+$  class,<sup>53</sup> so we can anticipate that re-entrant melting will occur for this model system and that we can definitely exclude clustering effects. For densities up to  $\rho\sigma^3 \sim 3$  we observe the first reentrant melting process: for  $Z \geq 200$  the liquid freezes—first into an fcc structure which then transforms into a bcc structure—and then remelts again. The RY and the HNC approximations give qualitatively similar results; on a quantitative level we note that HNC has the tendency to broaden the fcc/bcc region in the phase diagram, predicting freezing already for  $Z \geq 140$ . Upon further compression rather exotic and open structures (hexagonal, bco, and trigonal) emerge, a feature which is characteristic and meanwhile well known for systems with soft interactions (see also Refs. 50 and 41); these structures are stable for  $Z \geq 350$ . In this region of the phase diagram the RY and the HNC results agree now also on a *quantitative* level: obviously the mixing parameter in the RY closure leads to a complete suppression of the PY component and we can conclude that HNC gives

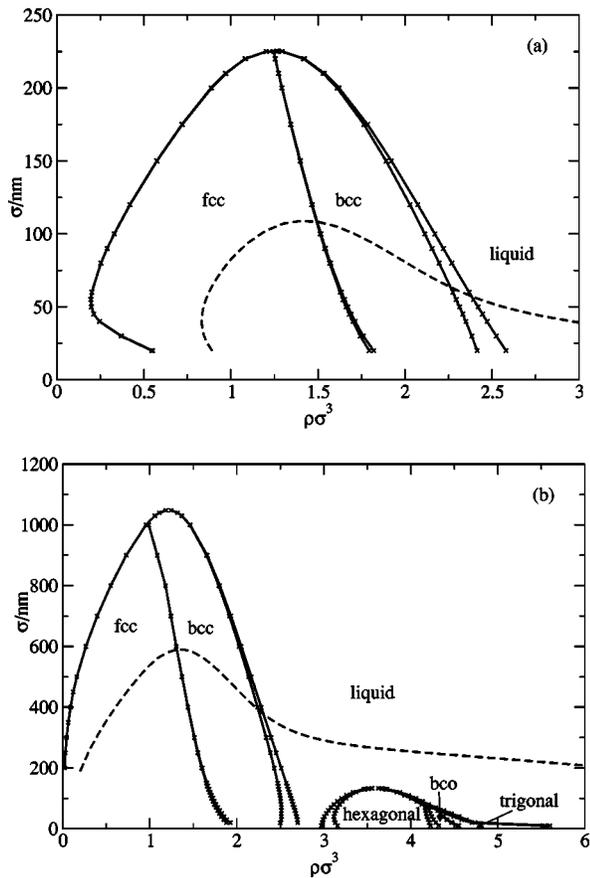


FIG. 8. Phase diagrams on the  $(\rho, \sigma)$  plane for fixed values of  $Z$ . (a)  $Z=200$  and (b)  $Z=400$ . Here the fluid free energy has been obtained through the HNC closure. The Hansen–Verlet locus is also shown as a dashed line.

thermodynamically self-consistent and therefore accurate results. Compared to the low density part this region of the phase diagram is considerably more complex and diversified (see insets of Fig. 7): this points out that the energies of the competing crystal structures are very close to each other.

We finally focus on the small liquid gap at  $\rho\sigma^3 \sim 3$  between the bcc and the hexagonal structures. Despite considerable efforts we are not able to predict the topology of the phase diagram in this density range for higher charges: on the one side we encounter convergence problems to solve the integral equations [values of the main peak in  $S(q)$  of  $\sim 10$  have been obtained], on the other side the validity of the model breaks down for such high  $Z$  values; thus a closer analysis of this region of the phase diagram is out of reach.

The broken lines in Figs. 7 and 8 locate those states of the system, where the value of the main peak of the static structure factor of the fluid phase,  $S(q_0)$  assumes a value of 2.85. Passing this value represents a classical and well-tested indication for an incipient freezing transition in repulsive systems, the Hansen–Verlet rule.<sup>38,54</sup> From our results it becomes evident that this criterion can only be used for smaller densities, i.e., up to approximately the overlap density  $\rho_*$  where the broken lines lie close to the freezing lines. Beyond  $\rho_*$ , the Hansen–Verlet criterion clearly fails: the broken lines lie deeply in the liquid phase region of the phase diagram, i.e., far away from the freezing transition. We can conclude that the Hansen–Verlet freezing rule is applicable for our system only for densities below  $\rho_*$ .

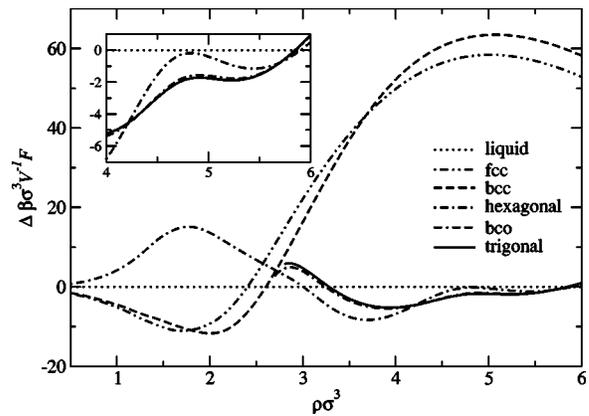


FIG. 9. Free energy difference per particle between the various solid phases and the fluid for  $Z=600$ . The fluid free energy has been calculated by means of the HNC closure. The inset shows a detail of the main plot at the region of high densities.

The salient features of the phase diagram are typical for the class of systems that have been termed *ultrasoft colloids*<sup>55</sup> and shows striking similarities with the previously obtained phase diagrams of charged, polyelectrolyte stars<sup>41</sup> and neutral star polymers.<sup>50</sup> Below the overlap density, we encounter the crystallization into the fcc lattice, which is due to the Yukawa tail of the interaction potential. Upon further increase of the density, the Yukawa interaction becomes softer, due to the absorption of counterions inside the microgel, causing thereby a transition into the bcc lattice. The same effect has been seen in the phase diagram of polyelectrolyte stars.<sup>41</sup> For neutral star polymers, where the pair potential is density-independent, the fcc-bcc transition takes place when the functionality  $f$  of the stars is changed, since  $1/f$  formally plays there the role of the Debye screening length in the Yukawa interaction. The remelting of the bcc crystal upon increasing the density beyond its overlap value, as well as the unusual crystal structures thereafter are caused by the ultrasoft effective potential for strong overlaps. The fact that the crystal types themselves and their sequence of appearance in the phase diagram differs from the other, previously examined ultrasoft systems,<sup>41,50</sup> shows that the details of the ultrasoft interactions are relevant for the stabilization of particular lattice structures.

In Fig. 8 we show phase diagrams for ionic microgels for two different values of  $Z$  in the  $(\sigma, \rho\sigma^3)$  plane; the properties of the liquid phase have now been calculated within the HNC approximation. For  $Z=200$  only freezing into an fcc and a bcc structure is observed, followed by a reentrant melting process close to  $\rho_*$ . The situation is considerably more complex for  $Z=400$ , as could already be expected from Fig. 7: in particular, for small  $\sigma$  values (i.e.,  $\sigma \lesssim 50$  nm) and intermediate to high densities, freezing into a hexagonal, a bco, and a trigonal structure with a subsequent re-entrant melting is observed.

In Fig. 9 we show the free energy differences between the fluid phase and the crystal structures encountered in the phase diagram for  $Z=600$  and  $\sigma=100$  nm; the properties of the fluid phase have been calculated within the HNC approximation. From this figure one can easily see the stable phases as the density is increased: first fcc, then bcc, fol-

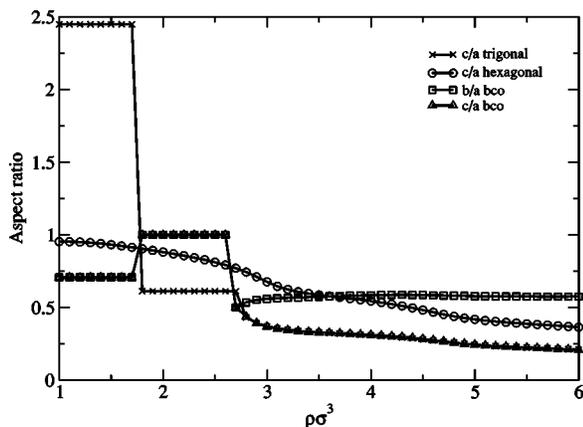


FIG. 10. Representative results for the aspect ratios of the conventional unit cells of the various crystal structures. Shown here are results for  $Z=600$ .

lowed by the small corridor of a stable fluid phase for  $\rho\sigma^3 \sim 3$ . Then follows the part of the phase diagram where the more exotic crystal structures (hexagonal, bcc, trigonal, and hexagonal again) emerge; note that—as one can also see from the inset—the energy differences between the competing phases are now considerably smaller than between fcc and bcc. For  $\rho\sigma^3 \geq 6$  the system remelts again.

In Fig. 10 we display—as a quantitative analysis of the crystal structures encountered in the phase diagrams—aspect ratios of the trigonal ( $c/a$ ), the hexagonal ( $c/a$ ), and of the bcc ( $b/a$  and  $c/a$ ) lattices for  $Z=600$  and  $\sigma=100$  nm. We point out that the trigonal lattice for densities up to  $\sim 1.8$  with an aspect ratio of  $c/a \equiv \sqrt{6}$  is equivalent to the fcc structure and that the trigonal lattice for densities  $1.8 \leq \rho\sigma^3 \leq 2.6$  with  $c/a \equiv \sqrt{3/8}$  is equivalent to the bcc lattice. In Fig. 10 one easily recognizes the transition densities of fcc  $\rightarrow$  bcc and bcc  $\rightarrow$  hexagonal (via the fluid phase) by the discontinuities in the aspect ratio curves. Note the agreement between the  $c/a$  ratio for the bcc and the trigonal structure for  $\rho\sigma^3 \geq 2.7$ : this reflects the fact that both structures have large similarities in their first coordination shells (see also the results for the star polymers<sup>50</sup>).

Finally, in Fig. 11 we display the Lindemann ratios  $L$ . The latter is defined as the ratio between the root-mean-

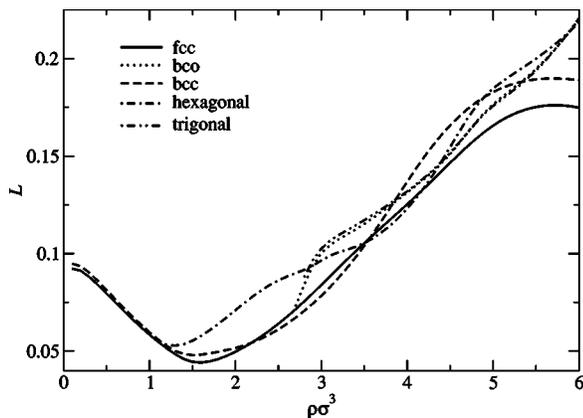


FIG. 11. The Lindemann ratios of the various crystal structures as a function of the density for  $Z=600$ .

square displacement of a particle from a lattice cite, due to the harmonic oscillations, over the nearest-neighbor distance  $a$ . The parameter combination chosen is  $Z=600$  and  $\sigma = 100$  nm for the five different candidate structures as functions of the density. For classical crystals of particles that interact by means of steeply repulsive interactions, a Lindemann ratio of 10 to 13% indicates an incipient melting transition.<sup>56</sup> We see that this criterion is still valid for  $\rho\sigma^3 \lesssim 3$ , i.e., where the classical freezing structures fcc and bcc are encountered. However, as we increase the density and as we proceed to the more open structures, the Lindemann ratios of these structures clearly pass this threshold. It is expected, of course, that for the highly anisotropic exotic structures at high densities, the Lindemann ratios along the various lattice directions will show a corresponding anisotropy. Nevertheless, even for the more isotropic fcc and bcc crystals, the Lindemann ratios show a clear increase at high  $\rho$  values, an indication of the softening of the crystals that become more delocalized. Further, although fcc and/or bcc have over the entire density range investigated the smallest  $L$  values, they do not represent the stable structures: instead, in the high-density region strongly anisotropic structures have been found to be the stable ones.

From these considerations, the following conclusions can be drawn: (i) we confirm earlier results that for ultrasoft interactions highly asymmetric structures are found to be specific in the intermediate- and high-density region of the phase diagram. The arguments that have justified closed packed structures in systems with harshly repulsive interactions have to be reconsidered thoroughly: due to the relatively small energy penalty for short interparticle distances in systems with bounded potentials it is from the energetic point of view more attractive to first build a shell of a few neighbors at rather short distances and then a second shell of particles at rather remote distances. This explains why the anisotropic, exotic crystals with a small number of nearest neighbors are preferred in freezing processes at high densities. (ii) It therefore does not surprise that the well tested and established freezing rules (due to Hansen and Verlet or based on the Lindemann ratio) are valid only in a restricted part of the phase diagram and can no longer be used to predict freezing transitions in the entire phase space: above the overlap density  $\rho_*$  these traditional melting/freezing criteria are violated. We take these two findings as indications that a rich variety of unexpected new phenomena is still waiting to be discovered in the physics of systems with soft interactions.

## VI. INFLUENCE OF THE STERIC INTERACTIONS

Up to now, the steric repulsion that is due to the overlap between the monomer units of two interacting microgels has been ignored and the analysis has been carried out exclusively on the basis of the electrostatic and counterion-induced interactions between the macromolecular aggregates. We will now add to the effective potential, Eqs. (3)–(5), the steric repulsions. In agreement with the derivation of the electrostatic interactions in Ref. 31, we model the microgels as homogeneous spheres of diameter  $\sigma$ , each being characterized by a monomer volume fraction  $\phi$  in its interior.

Within the framework of standard Flory–Huggins theory,<sup>1</sup> the steric free energy  $\mathcal{F}_{\text{st}}^{(1)}$  associated with a single microgel particle is given by the relation

$$\mathcal{F}_{\text{st}}^{(1)} = \frac{V_0}{v_c} k_B T \left( \frac{1}{2} - \chi \right) \phi^2, \quad (13)$$

where  $V_0 = \pi\sigma^3/6$  is the volume of the microgel particle,  $v_c$  is the typical volume occupied by a monomer, and  $\chi$  is the Flory–Huggins parameter characterizing the solvent quality, with  $\chi=0$  representing an athermal solvent and  $\chi=1/2$  a  $\Theta$  solvent.

Generalizing now the Flory–Huggins arguments to two overlapping microgels separated by a distance  $D \leq \sigma$ , we can derive the associated steric free energy  $\mathcal{F}_{\text{st}}^{(2)}(D)$  as

$$\mathcal{F}_{\text{st}}^{(2)}(D) = \frac{2V_0}{v_c} k_B T \left( \frac{1}{2} - \chi \right) \phi^2 \left[ 1 - \frac{3}{2} \left( \frac{D}{\sigma} \right) + \frac{1}{2} \left( \frac{D}{\sigma} \right)^3 \right] + 2\mathcal{F}_{\text{st}}^{(1)}. \quad (14)$$

Accordingly, the steric interaction  $v_{\text{st}}(D) = \mathcal{F}_{\text{st}}^{(2)}(D) - \mathcal{F}_{\text{st}}^{(2)}(\infty) = \mathcal{F}_{\text{st}}^{(2)}(D) - 2\mathcal{F}_{\text{st}}^{(1)}$  takes the form

$$\beta v_{\text{st}}(D) = \begin{cases} \alpha \left[ 1 - \frac{3}{2} \left( \frac{D}{\sigma} \right) + \frac{1}{2} \left( \frac{D}{\sigma} \right)^3 \right], & D \leq \sigma; \\ 0, & D > \sigma, \end{cases} \quad (15)$$

where the dimensionless prefactor  $\alpha$  is given by the relation

$$\alpha = \frac{2V_0}{v_c} k_B T \left( \frac{1}{2} - \chi \right) \phi^2. \quad (16)$$

The typical size of swollen, ionic PNIPAM microgels lies in the range  $100 \text{ nm} \leq \sigma \leq 600 \text{ nm}$ . We fix  $\sigma = 100 \text{ nm}$  in order to compare the phase diagrams that include the steric interaction with the one shown in Fig. 7, which is based on the electrostatic potential alone, and for which the same value of  $\sigma$  was chosen. For ionic PNIPAM microgels, the typical monomer volume fraction lies in the range  $10^{-3} \leq \phi \leq 6 \times 10^{-2}$ , see Table 2 in Ref. 10. In order to estimate the “monomer volume”  $v_c$ , we have to take into account the Manning-condensed counterions that form “bound pairs” with the backbones of the chains. It has been shown<sup>57</sup> that a good estimate is  $v_c = 30\ell^2$ , with the typical monomer length  $\ell \approx 3 \text{ \AA}$ . Using Eq. (16), we estimate the range of values for the parameter  $\alpha$  to be

$$\left( \frac{1}{2} - \chi \right) \leq \alpha \leq 200 \left( \frac{1}{2} - \chi \right), \quad (17)$$

where  $0 \leq \chi \leq 1/2$ .

We now consider the total interaction potential  $v_{\text{tot}}(r) = v_{\text{eff}}(r) + v_{\text{st}}(r)$ , where  $v_{\text{eff}}(r)$  is given by Eqs. (3)–(5) and  $v_{\text{st}}(r)$  by Eq. (15) above. As representative values for the prefactor  $\alpha$  we choose  $\alpha = 100$  and  $\alpha = 50$  and we redraw the phase diagrams following the same procedure described before. The resulting phase diagram for  $\alpha = 100$  is shown in Fig. 12. It can be seen that for sufficiently large values of the charge  $Z$  (i.e.,  $Z \geq 150$ ), the steric interaction has practically no influence on the phase boundaries, since the electrostatic one, which scales with  $Z^2$ , dominates. For low charge values, however, the steric interaction causes freezing into fcc and bcc lattices in the region in which the electrostatic interaction

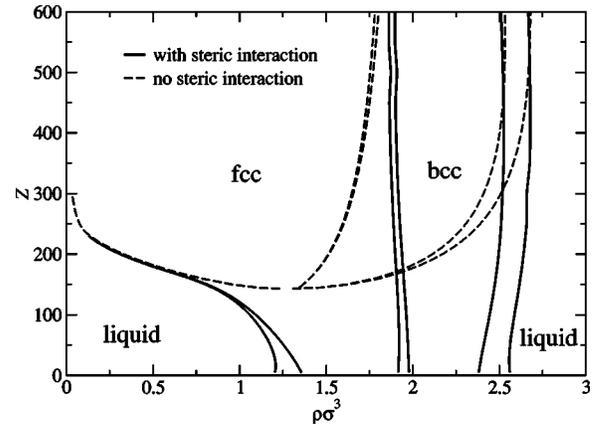


FIG. 12. The phase diagram of ionic microgels with diameter  $\sigma = 100 \text{ nm}$ , including now the steric interaction of Eq. (15). Here, the prefactor  $\alpha$  in Eq. (16) has the value  $\alpha = 100$ . Notice the extension of the intervening fcc and bcc phases to  $Z=0$  and the resulting separation of the domain of stability of the fluid into two disconnected regions.

alone cannot support any crystalline phases. As a matter of fact, the topology of the phase diagram is altogether modified, in the sense that the stable fluid region is now broken up into two fluid stability domains separated by a fcc region that is followed by a bcc one, as the density grows at fixed  $Z$ . The influence of the steric repulsion, therefore, is to extend the region of stability of the solid phases. This is also demonstrated in Fig. 13, pertaining to  $\alpha = 50$ , where it can be seen that the steric repulsion is not strong enough to alter the topology of the phase diagram; however, a growth of the stability regions of the crystals takes place nevertheless. Another consequence of the introduction of the steric part in the effective potential is a broadening of the stability region of the fcc lattice against the bcc. This is clearly due to the increased repulsion of the interaction potential, an effect that favors the formation of close-packed structures. The critical value  $\alpha_c$  for which the fluid region is split up into two disconnected domains has been found to be  $\alpha_c \approx 70$ .

## VII. SUMMARY AND CONCLUDING REMARKS

We have examined in detail the structural and phase behavior of spherical, ionic microgels, which form a member

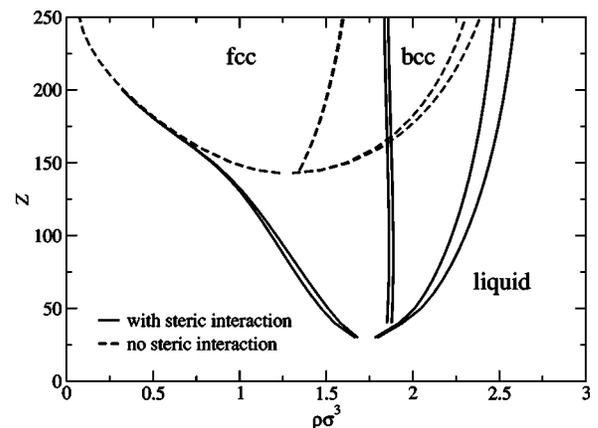


FIG. 13. Same as Fig. 12 but for a value  $\alpha = 50$  of the prefactor in Eq. (15). Notice that the fluid region remains connected but the regions of stability of the fcc and bcc lattices are extended.

of the class of ultrasoft colloids. This character is manifested in their effective interaction potential, whose soft and bounded character lies in the heart of a host of characteristic properties of such systems: anomalous correlation functions, reentrant melting regions and unusual crystal phases. Since the crystalline symmetry of the solids stabilized by such interactions is not cubic and the usual arguments that are based on hard-sphere mappings and the concomitant close-packed structures do not apply for such interactions, an extended search over a large variety of crystalline arrangements is necessary. To this effect, the evolutionary algorithm employed and presented in this work, provides a reliable and efficient tool to predict the equilibrium structures of the system, once an accurate scheme for the estimate of their free energies is available.

Our findings should be verifiable in experiments using loosely cross linked and highly charged microgel particles, whose synthesis is practicable with modern chemical techniques. We also anticipate that, in analogy with star-polymer solutions that show a similar topology of their equilibrium phase diagram,<sup>50</sup> ionic microgels may display unusual non-equilibrium glass behavior,<sup>58</sup> including reentrant liquification or melting by addition of free homopolymer chains.<sup>59</sup>

## ACKNOWLEDGMENTS

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## APPENDIX: ON THE RELATION BETWEEN THE VOLUME TERMS FOR PENETRABLE MICROGELS AND FOR IMPENETRABLE COLLOIDAL SPHERES

In Ref. 33, linear response theory, which is formally identical to the approach of Ref. 31, has been applied to derive effective interaction potentials and the volume term of charge-stabilized colloidal suspensions consisting of hard, charged colloidal particles (charge  $Ze$ ), their corresponding counterions and possibly salt. The volume term  $\Phi_0$  there reads for the salt-free case as<sup>33</sup>

$$\Phi_0 = ZNk_B T [\ln(Z\rho\Lambda^3) - 1] - \frac{(Ze)^2}{2\epsilon\sigma} \frac{N\kappa\sigma}{1 + \kappa\sigma/2} + k_B T \frac{\eta}{1 - \eta} \frac{2n_+n_-}{n_+ + n_-} - ZN \frac{k_B T}{2}, \quad (\text{A1})$$

where  $N$  is the number of colloidal particles in the solution,  $\sigma$  is their diameter,  $n_{\pm}$  are the number densities of the positively/negatively charged species,  $\kappa$  is given by Eq. (6), and  $\eta$  is defined as

$$\eta = \frac{\pi\rho\sigma^3}{6}, \quad (\text{A2})$$

with the density  $\rho$  of the colloidal particles. A comparison of Eq. (8) with Eq. (A1) shows that the two volume terms are different, a manifestation of the physical discrepancy be-

tween the two systems: the microgels are penetrable to the counterions but the colloids are not. Nevertheless, in the mathematical limit of vanishing spatial extent of the colloids<sup>60</sup> and the microgels ( $\sigma \rightarrow 0$  for both), the two expressions, Eqs. (8) and (A1) should coincide. For Eq. (A1) we easily obtain

$$\lim_{\sigma \rightarrow 0} \Phi_0 = ZNk_B T [\ln(Z\rho\Lambda^3) - 1] - N\kappa \frac{(Ze)^2}{2\epsilon} - ZN \frac{k_B T}{2}. \quad (\text{A3})$$

If we now naïvely take the  $\sigma \rightarrow 0$  limit in Eq. (8), however, we do not obtain an expression identical to Eq. (A3) above. In order to resolve this apparent inconsistency, we first note that the volume term  $E_0$  is defined as [see Eq. (14) in Ref. 31]

$$E_0 = ZNk_B T [\ln(Z\rho\Lambda^3) - 1] + \frac{N}{2} \lim_{r \rightarrow 0} v_{\text{ind}}(r) + N\rho \lim_{k \rightarrow 0} \left[ -\frac{1}{2} \hat{v}_{\text{ind}}(k) + Z\hat{v}_{\text{mc}}(k) + \frac{Z^2}{2} \hat{v}_{\text{cc}}(k) \right], \quad (\text{A4})$$

with the Fourier transforms  $\hat{v}_{\text{ind}}(k)$ ,  $\hat{v}_{\text{mc}}(k)$ , and  $\hat{v}_{\text{cc}}(k)$  of the induced, microgel-counterion, and counterion-counterion interactions, respectively. In going from the general Eq. (A4) to Eq. (8) of the main text, the limits  $r \rightarrow 0$  and  $k \rightarrow 0$  have been taken while  $\sigma$  is held fixed at a finite value. When we consider the limiting case of vanishing microgel extent, the limit  $\sigma \rightarrow 0$  must be taken *before* the limits  $r \rightarrow 0$  and  $k \rightarrow 0$  are carried out. With the help of Eqs. (34) and (40) of Ref. 31 and taking into account that  $\hat{v}_{\text{cc}}(k) = 4\pi e^2 / (\epsilon k^2)$ , we first find that the third term in Eq. (A4) yields the corresponding third term in the right hand side of Eq. (A3), whereas the second term takes the form:

$$\lim_{r \rightarrow 0} \lim_{\sigma \rightarrow 0} v_{\text{ind}}(r) = -\frac{4\pi(Ze)^2}{\epsilon} \frac{1}{(2\pi)^3} \int d^3k \frac{\kappa^2}{k^2(k^2 + \kappa^2)} = \kappa \frac{(Ze)^2}{\epsilon}. \quad (\text{A5})$$

Introducing the last result into Eq. (A4) above, we obtain the second term of Eq. (A3) and the equality  $\lim_{\sigma \rightarrow 0} E_0 = \lim_{\sigma \rightarrow 0} \Phi_0$  is established.

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