1 Introduction

Fundamental physics requires experiments to observe, and theory to explain. In principle, nothing more is needed for a complete understanding of the phenomena. However, in some situations, this sharing of the work is not sufficient, either because the experimental data are counter-intuitive (disagreement with the theory) or because the theory itself is impracticable. If one of these case arises, numerical simulations turn out to be the essential tool to complement our ideas through direct ‘observation’ of the theory or through artificial changes of the microscopic rules (as in a Maxwell’s demon-like approach to analyze the cause-to-effect mechanisms).

In the present article, we discuss results of numerical simulations dedicated to the comprehension of recent experiments in which a dispersion of polydisperse repulsive nanoparticles was compressed through osmosis. Details of the experiments will be published elsewhere. A suspension of ordinary colloidal silica particles (Ludox, polydispersity 14%, average radius 8 nm), was compressed through dialysis. This caused a spontaneous segregation of the particles, fractionated crystallization and multiple-phases coexistence (involving various crystal structures). For instance, the low-compression part of the phase sequence was seen to be: colloidal liquid at the lowest volume fractions, then nucleation of the BCC crystalline phase at a silica volume fraction $\phi > 0.19$, and then coexistence of BCC + Laves AB$_2$ crystal phases for $\phi > 0.22$. The complete phase diagram was found to be much richer than expected according to current theories.

It is important to note that we do not describe here ordinary fractionated crystallization caused by different solubilities of co-existing substances, but a new kind of fractionation that organizes populations of particles with different sizes, and makes the best use of available space. Without any theory at hand to explain the formation of such uncommon structures as the Laves AB$_2$ crystals, we used the Gibbs-ensemble Monte-Carlo method to understand the mechanisms used by the system to sort the various particle sizes and to put them in the correct places.

Actually we encountered many unanswered questions from the experimental data. The numerical simulations helped us to answer some of them. We replicate hereafter this particular state of mind, dividing our comprehension process in a series of short questions and discussing the answers given by the numerical study. The reader interested in a quantitative comparison between the experimental data and the numerical simulations should refer to

To close this Introduction, let us give a warning which might be important when comparing experimental data with numerical simulations: the regular Monte-Carlo method does not consider real kinetic processes, but is the efficient tool to search for the equilibrium state using the physical ground of free energy minimization. Then, the results presented below are linked to the equilibrium state. If it is not the case (in experiments, in kinetic numerical simulations), other intermediate crystalline structures may appear for some time as unstable phases.

2 The system under study

We consider a dispersion of spherical hard particles. The surface of each particle is electrostatically charged with 0.4 $e$ / nm$^2$. The particle radius is denoted: $a$, and its value is Gaussian-distributed with the average value $\langle a \rangle = 8$ nm and standard deviation $\sigma$, truncated to the range: [4 nm ; 12 nm] (that is: no radius is smaller than 4 nm or larger than 12 nm). The polydispersity, $\delta$, of this population is defined as: $\delta^2 = \langle a^2 \rangle / \langle a \rangle^2 - 1$. Then, the value of $\delta$ coincides with $\sigma / \langle a \rangle$ for the small values of $\sigma$, and has the limiting value $1 / \sqrt{12} \approx 29\%$ for the infinite value of $\sigma$ (rectangular distribution). Throughout the article, we shall take the value $\sigma = 1.2$ realizing the polydispersity $\delta = 15\%$ of the population.
If large polydispersity (say $\delta > 25\%$) has to be considered, the influence of moments of order larger than 2 should be studied, that is to investigate various distributions – such as log-normal or Schulz distributions – with the same values of $(a)$ and $\delta$. In related problems, the shape of the radius-distribution is known to be unessential.\(^4\)

We consider here the DLVO theory\(^5\), in which the interaction energy between two charged particles, labelled $i$ and $j$, is generally of the Yukawa (screened-Coulomb) form:

$$U_{ij}/k_B T = Z_i Z_j \frac{Q_i Q_j}{r_{ij}} e^{-\kappa r_{ij}}, \quad \text{for} \quad r_{ij} \geq a_i + a_j \quad (1)$$

where $Z_i$ is the effective charge of the particle $i$, and $r_{ij}$ the distance between their centers. $l_D = 0.7$ nm is the Bjerrum length, and $\kappa = 1/l_D$ is the screening parameter, with $l_D = 3$ nm the Debye screening length in our experimental conditions. The values of $l_D$ and $l_P$ are expected to be constant throughout the system.

Two definitions have to be stated:

- the energy at contact (i.e. using (1) for $r_{ij} = a_i + a_j$), traditionally written: $\beta e$, is a central parameter for discussion. Its averaged value is $\beta e = 21.6$ for the present set of parameters

- the potential energy per particle at equilibrium is here denoted generically: $E$. It is defined as the sum of the pair-potentials (1) between all the couples of particles forming the equilibrated system, divided by the total number of particles, after having minimized the system free-energy using the Monte-Carlo method.

At small or intermediate volume fractions – namely: $\phi \leq 0.41$ for $\delta = 15\%$, the Wigner-Seitz radius is larger than $(a) + l_D$. In these conditions, the attractive Van der Waals interaction between silica spheres in water is smaller than the thermal energy, $k_B T$, then can be neglected. In the same way, we do not discuss here controversial additional weak long-ranged attractive pairwise potential such as appearing in the Sogami-Ise theory\(^6\).

Within our approach, such interaction would result in the same shape of the radius-distribution. The influence of moments of order larger than 2 should be studied, especially in the case of strong repulsive DLVO potential, with $\kappa$ a few order of magnitude larger than the screening length in our experimental conditions. The values of $l_D$ and $l_P$ are expected to be constant throughout the system.

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To know the thermodynamic equilibrium of the system, we use a variant of the Gibbs ensemble Metropolis random exchanges of particles, introduced to study the thermodynamic evolution of different phases coexisting in a liquid.\(^5\) Particles are exchanged randomly between the phases according to the usual Metropolis Monte-Carlo scheme, keeping any time constant the total number of particles, the total volume of the system and the temperature. In this method, the homogeneous coexisting phases are simulated in separated boxes without interfaces between the phases, and each box is with periodic boundary conditions. Particle exchanges occur either inside a single phase, or from different phases.

To make the approach more efficient, we sample the configuration space into a finite number of configurations, for example taking the 19 configurations corresponding to the coexistence of one cubic BCC crystal and one cubic FCC crystal, the total sum of the sites being in between 3500 and 4500 (in order to compare systems of about the same total sizes). When thermodynamic equilibrium is reached in every configuration, the total energy, \(E\), of the system is evaluated for each configuration. The program is then scanning little by little the energy landscape of (a sampling of) the configuration space, and the approximate partition function \(Z = \sum_{\text{conf}} \exp(-E/k_B T)\) gives access to all thermodynamic quantities at equilibrium. The average value of the proportion of the BCC phase at equilibrium is estimated through:

\[
\langle \rho_{\text{BCC}} \rangle = \frac{1}{Z} \sum_{\text{conf}} \rho_{\text{BCC}} e^{-E/k_B T} \tag{2}
\]

and similarly for \(\langle \rho_{\text{FCC}} \rangle\).

Let us discuss the results for the value \(\phi = 0.3\) realizing the equality of the pure BCC and pure FCC energies, as seen on the Fig.1. As it could be expected, \(\langle \rho_{\text{BCC}} \rangle = \langle \rho_{\text{FCC}} \rangle = 0.5\) is obtained in this case because of the choice \(E_{\text{BCC}} = E_{\text{FCC}}\) for the pure phases. However, the actual value of the energy per particle for BCC and FCC crystals of the same size, is found to be \(E = 22.2\ k_B T\), significantly lower than the value for the single phase \(E_{\text{BCC}} = E_{\text{FCC}} = 23.0\ k_B T\). This means that the system put different particle distributions in the different phases. This happening is exemplified in the Fig.2 where the at-equilibrium radius distributions in the two phases are compared for the configuration corresponding to the BCC crystal of 2000 sites, and the FCC crystal of 2048 sites. The radius-distribution in the FCC phase has approximately the Gaussian shape with polydispersity 6.5%, that is much smaller then the polydispersity (15%) of the total distribution including all the particles in the system. Consequently, both wings of the initial Gaussian distribution distribute in the BCC phase.

5 Q3: why does the BCC crystal accept handling two modes of particle radius while FCC sticks to one mode?

A3 : the detailed management of the initial radius-distribution by the system results from the different abilities of the phases to accept particles of different radii (that is here: of different electric charges). Following this idea, one can define a parameter of tolerance as the maximum relative decrease of the system energy when changing the charges of a couple of particles, keeping the total charge unchanged. More precisely, let us define the tolerance, \(\tau\), by the expression:

\[
\tau = \min \left\{ -\frac{\Delta E}{U_o} \right\} \tag{3}
\]

in which \(\Delta E\) is the variation of the system energy when the charges of two particles are changed from the initial values \(Z\) to \(2Z\) and 0, respectively, and \(U_o = Z^2 k_B T\) is a reference energy for the system. The minimum value in (3) is taken over all the possible positions of the couple of particles with modified charge. This concept supposes that the system is able to detect the best (from the point of view of the energy) relative positions of the two concerned particles. Then the repulsive interactions are expected to be long-ranged - as the Yukawa potential is - even if the characteristic lengths are finite. For a regular lattice with only one sort of sites, the value of \(\tau\) is given by the expression:

\[
\tau = \frac{e^{-r_0}}{k_B T} \tag{4}
\]

where \(r_0\) is the value of the distance between nearest neighbours.

For the BCC lattice of volume fraction \(\phi\), one has \(r_0/a = (\pi \sqrt{3}/3\phi)^{1/3}\), and for the FCC lattice at the same volume fraction: \(r_0/a = (\pi \sqrt{2}/3\phi)^{1/3}\). Then, \(\tau_{\text{BCC}} > \tau_{\text{FCC}}\) for all values of \(\phi\) (for \(l_0 = 3\ nm\) and \(\alpha = 8\ nm\) considered here: \(\tau_{\text{BCC}}/\tau_{\text{FCC}} = 1.3\), for \(\phi = 0.3\)). This indicates that the FCC crystal is less tolerant than BCC, or, equivalently, that changing the charges of two particles following: \(Z \rightarrow 2Z\), and \(Z \rightarrow 0\) results in a larger decrease of the BCC lattice energy than in the FCC case.
This is the reason why, from the point of view of the energy, the system prefers to fill the FCC lattice with particles of almost the same charges, and to arrange the rest of the particles on the BCC lattice.

As a conclusion, we propose here the ‘tolerance rule’ under the form: in the case of coexistence of several phases, the less tolerant phase prevails over all the other phases in the distribution of the radii.

6 Q4: which information can the method give about experiments of compression of a system of charged polydisperse particles?

A4 : as explained in the Introduction, we explored recently colloidal crystallization of polydisperse Ludox HS silica nanoparticles dispersed in water through near-equilibrium dialysis to achieve very slow compression of the polydisperse suspension. We demonstrated that, in charge-stabilized colloidal dispersions at intermediate compressions, the system exhibits two crystalline phases, namely: a BCC phase and a Laves AB2 phase, in coexistence with liquid. Moreover, the FCC phase is missing. The Laves AB2 crystalline system is known to be relevant for opal structure, and more generally for packing of bidisperse particles with radius ratio about 0.8, filling the less tolerant phase are distributed in the Gaussian shape with polydispersity smaller than the overall polydispersity δ of the system, that is: polydispersity favors the search for more tolerant phases. As previously, the ensemble average of the proportion of the less-tolerant phase at equilibrium, δ, is such that: τ_{BCC}/τ_{AB2} = 3.55, in the experimental conditions, then the Laves lattice is much more tolerant than FCC to accepting uneven particles. Therefore, an argument similar to the one developed in the Section B, leads to the conclusion that the BCC phase should collect most of the particles close to the mode of the radius-distribution, while the wings of the distribution should fill the AB2 phase.

To be more quantitative, the Gibbs ensemble Monte-Carlo method was used for the system made of a BCC phase in coexistence with a AB2 phase. As previously, the ensemble average of each crystalline phase proportion is evaluated after sampling the configuration space. It results in the ensemble-average values: ⟨τ_{BCC}⟩ = 0.52 : ⟨τ_{AB2}⟩ = 0.48 corresponding to the respective volume proportions of the phases at equilibrium. Then, considering the system close to these values, that is: a BCC crystal of 9 × 9 × 9 unit cells, and a Laves AB2 crystal of 5 × 5 × 5 unit cells, the resulting respective radius-distributions are plotted on the Fig.3.

Here too, we find that the less tolerant phase (the BCC phase in this case) collects most of the particles with radius close to the average radius. The final polydispersity of the BCC phase particles is 7.5% in this example, emphasizing the role of the repulsive interaction in the process, since that polydispersity exceeds significantly the terminal value 5.7% of the polydispersity of the crystal phase made of hard spheres colloidal particles precipitating from a fluid phase at equilibrium. Moreover, the AB2 phase is pretty well filled with particles with the particle-radius ratio about 0.8, the bigger particles being located in the octahedral sites, and the smaller ones in the tetrahedral sites.

This suggests a simple “rule of thumb” for the respective proportions of the two phases: suppose that the radii of the particles filling the less tolerant phase are distributed in the Gaussian shape with polydispersity smaller than the overall polydispersity δ of the system, and almost all the particles of radius ⟨r⟩ belong to this phase. Calculating the two modes of the remaining radius-distribution of the particles in the high-tolerant phase is then a simple exercise. If we constrain the ratio between the two radius modes to be $\sqrt{2/3}$ for the system to fit efficiently the AB2 phase, then one finds the relation:

$$\rho_B = \frac{\delta^*}{\delta}$$

with $\rho_B$ the proportion of the less-tolerant phase at equilibrium, and $\delta^* = 5 - \sqrt{24} \approx 10\%$. In (5), we approximated : $2\ln \rho_B/(1 - 1/\rho_B^2) \simeq \rho_B$.

Interpretation of the equation (5) is as follows: when $\delta < \delta^*$ the only less-tolerant phase (here : BCC) can exist ; when $\delta > \delta^*$, the proportion of the BCC phase is a decreasing function of the polydispersity, δ, of the system, that is: polydispersity favors the search for more tolerant phases.

It is worth noting that appearance of the Laves phase in this context can be related to a work on bidisperse particles. Indeed, such complex crystal structures were found to be spontaneously stabilized in the case of mixtures of spherical particles with two different diameters, interacting via simple repulsive potentials. This was shown by numerical simulations using the thermodynamic integration technique. However, our case is a priori...
much more surprising since there is not, at the beginning, any ‘magic’ radii ratio.

7 Q5: how long-ranged should the interaction be between the particles?

A quick answer is given considering the monodisperse case for the BCC or FCC lattices. In these cases, one knows the analytical formula for the energy per particle as a series in the orders of the energies, and then it is easy to compare the energy when only the nearest-neighbors are considered. For the same parameters as in the caption of the Fig.1 and \( \phi = 0.3 \), the only first-neighbors give the results: \( E_{\text{BCC}}^{(1)}/k_B T = 24.98 \) < \( E_{\text{FCC}}^{(1)}/k_B T = 29.79 \), which seems to show that the BCC crystal is more stable than the FCC crystal. But including the second-neighbors turns round that conclusion, as: \( E_{\text{BCC}}^{(2)}/k_B T = 30.47 > E_{\text{FCC}}^{(2)}/k_B T = 30.32 \). Taking into account all the neighbors confirms the latter conclusion: \( E_{\text{BCC}}^{(8)}/k_B T = 30.82 > E_{\text{FCC}}^{(8)}/k_B T = 30.51 \). Actually, this discussion was about the point \( \delta = 0 \); \( \phi = 0.3 \): \( (E_{\text{FCC}} - E_{\text{BCC}})/k_B T = -0.31 \) of the Fig. 1. Then, even if \( 1/d_{\phi} < 1 \), one must consider more than the only nearest-neighbors to get the correct conclusion about stability of the crystals.

To check the relevance of this ‘long-range versus short-range’ question in the case of the coexistence of BCC and AB\(_2\) phases of polydisperse particles, we cut the Yukawa potential (1) right after the first nearest-neighbors (three kinds of sites are to be considered: one for the BCC lattice, the tetrahedral site and the octahedral site of the AB\(_2\) lattice). Then, the second- and farther neighbors of a given particle do not interact with it any more. The main results are conveniently visualized on the Fig. 4, after plotting the energies per particle of the system in phase coexistence versus the composition of the system (characterized by \( \rho_{\text{BCC}} = 1 - \rho_{\text{AB}2} \) and \( \rho_{\text{AB}2} \), as the respective volume proportions).

The conclusion is that the number of neighbors considered is relevant in the energy profile versus the composition of the system. In the example in the Fig. 4, the system is probably a pure BCC crystal if the Yukawa interaction is cut at the first-neighbors, while coexistence of BCC and AB\(_2\) phases is clear when all the neighbors are taken into account.

8 Conclusions – what did you learn from the method?

In the case of the fractionated crystallization, the Gibbs ensemble Monte-Carlo method does not predict the nature of the phases at equilibrium. However, it can provide essential help for a quantita-

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1 in principle, one should consider ratio of effective radii based on the energy density. This does not change the equation (5) but the value of the limit polydispersity \( \delta^* \) which generally depends on the system volume fraction.
polydisperisities. This description of the mechanisms is close to the idea by Pusey in a different context – idea which has been validated much later through numerical simulations and theoretical developments –, that suspensions of highly polydisperse hard spheres might crystallize by splitting the broad overall distribution into a number of narrower distributions, each of which being accommodated within a single crystalline phase.

We shall close this presentation with three discussions about the limitations of the numerical method.

- The method does not consider the real kinetics of the mechanisms, then reliability of the method for the large volume fractions may be questionable since movements of the particles can be hindered. However, for systems of spherical particles, repulsive interactions act as lubrication between the particles and generate ergodicity. In other words, local rearrangement of the particles (related to the system capability to reach thermodynamic equilibrium) is facilitated by the repulsive interactions, and more precisely by the value of the energy at contact. This is no more the case in the opposite situation of the attractive interactions, resulting generally in non-equilibrium patterns.

- In principle, the method cannot predict the phases at equilibrium, since it supposes to have a priori information – or to make guess – about the phases in coexistence. However, one should note that if large unit crystal cells is being formed in the system, no numerical kinetic method (e.g. molecular dynamics) can nowadays predict the phases, due to essential computing limitations.

- A last but fundamental question is the role of the liquid phase in coexistence with crystals. In principle, the same Gibbs ensemble Monte-Carlo method for a system of two crystal phases plus a liquid phase can be used if a fast-computing free energy method is at hand for the liquid phase. The optimized random-phase approximation (ORPA) is a good candidate for a systematic study. This approach could help to solve the similar problem with large polydisperisities. Indeed, in this case, the wings of the charge-distribution function are probably too wide to be incorporated in the only Laves AB2 phase, and the system should choose the liquid phase as a reservoir of unfitting particles (too large or too small), expressing the high tolerance of the liquid phase. However, experimental data for such systems with large polydispersity are scarce, and it is not clear whether such a system will choose intensively use of the liquid phase (i.e. melting the phases) or if it will find another crystalline structure with a still larger unit crystal cell.

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References