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Induced order and re-entrant melting in classical two-dimensional binary clusters

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Abstract. – A binary system of classical charged particles interacting through a dipole repulsive potential and confined in a two-dimensional hard-wall trap is studied by Brownian dynamics simulations. We found that the presence of small particles *stabilizes* the angular order of the system as a consequence of radial fluctuations of the small particles. There is an optimum in the increased rigidity of the cluster as function of the number of small particles. The small (*i.e.* defect) particles melt at a lower temperature compared to the big particles and exhibit a *re-entrant* behavior in its radial order that is induced by the intershell rotation of the big particles.

Introduction. – Melting and crystallization are fundamental processes in nature and have been widely studied. Charged particles systems like, *e.g.*, colloids [1] and dusty plasmas [2] display similar phase behavior as atoms and molecules with the added advantage that the micrometer size of the particles and their slower dynamics make them accessible for real space imaging [3]. Most of the previous research was directed towards one-component systems. Recently, in a theoretical study in ref. [4] the complexity of the system was increased by investigating systems with two types of particles of different radii and different effective charge confined in a parabolic trap. A recent experimental study [5] concentrated on oppositely charged colloidal particles confined in a cavity and found a remarkable diversity of new binary structures. In this letter we consider a finite size binary system of repulsive particles which are confined to move in two dimensions (2D). The circular hard-wall confinement potential competes with the 2D Wigner crystal structure [6] and leads to ring-like arrangements for the particles [7, 8]. Previously it was shown experimentally [9] and theoretically [10] that single component systems exhibit a remarkable re-entrant melting behavior. In the present binary system we assume a large difference in the size and "charge" of the particles and therefore the smaller particles can be considered as "defects" which disturb the order of the big particles [11]. We found that these defect particles have a pronounced effect on the melting behavior of the system and results in an unexpected stabilization of the ordered phase and a new re-entrant

melting behavior. The possibility of stabilization was also addressed in the theoretical study of ref. [4] in the case of few binary Coulomb clusters confined in a parabolic trap.

The present study is motivated by the experiment of ref. [12], where the melting behavior of a binary system of paramagnetic colloidal spheres (with different radii) confined in 2D circular cavities was studied. The coupling parameter could be tuned by changing the applied magnetic field strength. They found that: 1) the shell-like structure of the system depends strongly on the relative number of big (N_B) and small (N_S) particles, and 2) the melting process takes place in several stages where first the small particles and afterwards the big particles become delocalized.

Model system. – In our model, like the experiment of ref. [12], the particles are confined by a circular hard-wall potential ($V_P = 0$ for $r \leq R$ and $V_p = \infty$ at $r > R$). As in the experiment, the particles interact through a repulsive dipole potential $V(\vec{r}_i, \vec{r}_j) = q_i.q_j/|\vec{r}_i - \vec{r}_j|^3$, where $q_i = M_i\sqrt{m_0/4\pi}$ is the "charge" and $\vec{r}_i$ the coordinate of the i-th particle. For a given type of interparticle interaction and external confinement, only three parameters characterize the order of the system: the number of big particles N_B, the number of small particles N_S (also called defect particles) and the coupling parameter Γ. In the experiment the diameter of the big particles is twice the diameter of the small particles [12], therefore we have chosen the charge of the small particles to be 1/8 of the charge of the big particles. As a representative example we will discuss in the following the results for clusters with 16 and 17 big particles. We define the characteristic energy of the inter-particle interaction for dipole clusters as $E_0 = q^2/a_0^3$, where $a_0 = 2R/{N_B}^{1/2}$ is the average distance between the big particles. In the present calculation we define the coupling parameters as $\Gamma = q^2/a_0^3 k_B T$, where k_B is the Boltzmann constant and T the temperature of the medium.

The ratio of the particle velocity relaxation time *vs.* the particle position relaxation time is very small due to the viscosity of water and consequently the motion of the particles is diffusive and overdamped. In our simulations we will neglect hydrodynamic interactions. Following [13], we rewrite the stochastic Langevin equations of motion for the position of the particles as those for Brownian particles:

$$\frac{\mathrm{d}\vec{r_i}}{\mathrm{d}t} = \frac{D_i}{k_B T}\left\{\sum_{j=1}^{N}\frac{\mathrm{d}V(\vec{r_i},\vec{r_j})}{\mathrm{d}\vec{r}} + \frac{\mathrm{d}V_P(\vec{r_i})}{\mathrm{d}\vec{r}} + \frac{\vec{F_L^i}}{m_i}\right\}, \tag{1}$$

where D_i is the self-diffusion coefficient and m_i is the particle mass of the i-th particle, and $\vec{F_L^i}$ is the randomly fluctuating force acting on the particles due to the surrounding media. In the numerical solution of eq. (1) we took a time step $\Delta t \leq 10^{-4}/(nD_B)$, where $n = N_B/(\pi R^2)$ is the density of the big particles. The radius of the circular vessel is $R = 36\,\mu$m and the self-diffusion coefficient of the big particles $D_B = 0.35\,\mu\mathrm{m}^2/\mathrm{s}$ is taken from the experiment [12]. As the self-diffusion constant is inversely proportional to the particle diameter (from the Stokes-Einstein relation $D = k_B T/8\pi\nu a$, with ν the viscosity of the fluid and a the particle diameter) we took $D_S = 0.7\,\mu\mathrm{m}^2/s$ for the small particles.

Before starting the Brownian dynamics we find first the ground-state configuration using the Monte Carlo technique as in ref. [14].

In order to characterize the angular order of the system, we calculate the angular diffusion of the particles over a 30 min $\times$ 1000 time interval. The relative angular diffusion coefficient can be written as

$$D_\theta = \left\{\langle\Delta\theta(t)^2\rangle - \langle\Delta\theta(t)\rangle^2\right\}/t, \tag{2}$$

where $\langle\rangle$ refers to a time averaging, and the mean relative angular displacement rotation of the first shell $[\theta_1(t)]$ relative to the second $[\theta_2(t)]$ one is defined as $\Delta\theta(t) = [\theta_2(t)] - [\theta_1(t)]$.

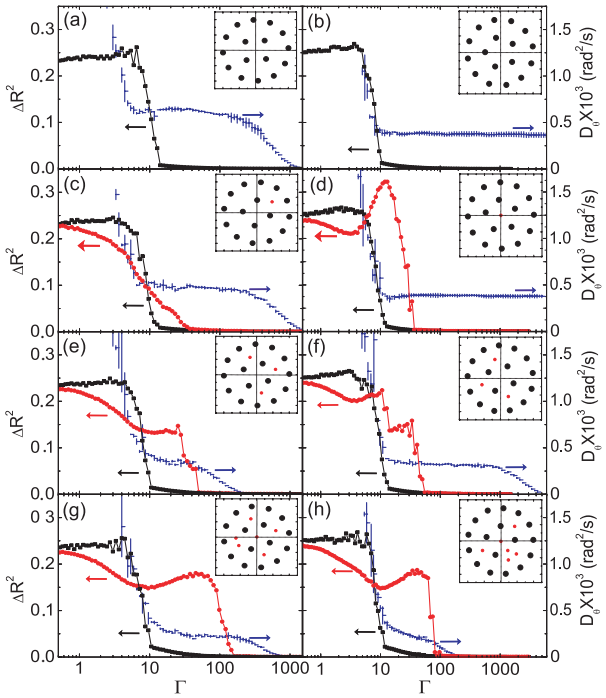

Fig. 1 – (Color online) Left column: system containing 16 particles. From top to bottom the number of small particles increases from 0, 1, 3, 6. Right column: system containing 17 particles. Right scale: the relative angular diffusion coefficient (given with error bars) as a function of Γ. Left scale: the ΔR^2 for the small particles (red bullets) and the big particles (black squares) in the binary cluster as a function of Γ. The insets show the corresponding ground-state configuration at $T = 0$.

The mean-squared radial diffusion (MSRD) coefficient is

$$\Delta R^2 = \frac{1}{N}\sum_{i=1}^{N}[\langle r_i(t)^2\rangle - \langle r_i(t)\rangle^2]/a_0, \tag{3}$$

which is a measure of the radial order in the system. The MSRD is calculated separately for the big and the small particles.

Results. – We found that all the interesting melting properties for small binary clusters are present in the $N_B = 16$ and $N_B = 17$ systems. In the insets of fig. 1 the ground-state configurations for these systems are shown with zero ((a) and (e)), one ((b) and (f)), three ((c) and (g)) and six ((d) and (h)) small particles. In a 16-particle system with less than 9 small particles (left column in fig. 1), one can see that the big particles form a shell structure with 4 particles in the inner shell and 12 particles localized at the edge of the hard wall. The small particles fill up the vacancies between the big particles. The difference of charge between the big particles and the small particles is so large, that the small particles are expelled from the outer ring. The (4,12)-configuration is a magic-number configuration and is exactly the same configuration as one finds without small particles [15]. (For 9 or more small particles the magic configuration is lost and the big particles form a non-magic configuration.) In a 17-particle system (right column in fig. 1) with no small particles, the big particles form the (5,12)-configuration. However, by adding 2 small particles to the system, the ground-state

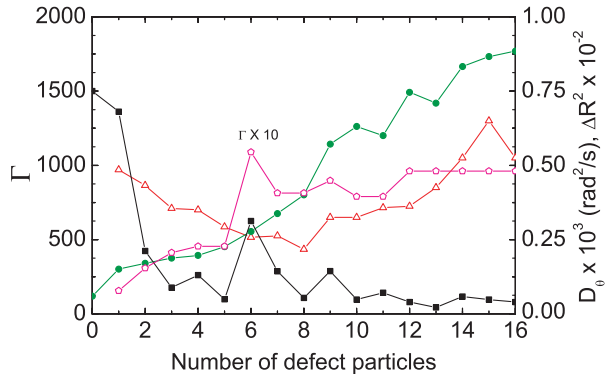

Fig. 2 – (Color online) System containing 16 particles. Black squares: critical Γ where the angular diffusion of the big particles is exceeding the value 100. Red triangles: height of the plateau of the angular diffusion curve measured at $\Gamma = 20$. Green dots: height of the ΔR^2 of the big particles measured at $\Gamma = 20$. Pink pentagons: Melt temperature of the small particles.

configuration of the big particles changes into the (4,13)-configuration. The reason for this change in the ground state is that the (5,12)-configuration is a non-magic–number configuration and by adding small particles the system tries to adjust to a more triangular lattice.

In order to study the melting of the binary clusters we performed Brownian dynamics simulations for several values of the coupling constant Γ. First, we show how the angular melting properties change by adding small particles. Afterwards, we deal with the radial melting properties.

Angular melting. The relative angular diffusion coefficients as a function of Γ for a system with 16 and 17 big particles for different number of small particles are shown in fig. 1. We notice from fig. 1(a), for the magic-number cluster (4,12) without small particles, that the relative angular diffusion curve starts to differ from zero around $\Gamma \approx 1000$. For larger values of Γ, both shells do not rotate relative to each other (*i.e.* they are locked), which is a typical behavior for a magic-number configuration. One can see that adding small particles influences drastically the relative angular melting temperature: the value of the coupling constant Γ at which the angular order between both rings is lost moves to smaller values. This is shown more clearly in fig. 2: the black squares show the Γ value at which the relative angular diffusion coefficient exceeds the value 100 as a function of the number of small particles in a cluster consisting of 16 big particles. One can see that adding even a few small particles can reduce the critical Γ value with a factor of ten. This leads to a first conclusion that *adding small particles stabilizes angular order* (*i.e.* it increases the rigidity of the cluster). This unexpected increase in angular order is induced by the vibrations of the small particles. The vibrating small particles, which are mostly situated between the inner and outer shell, lock both shells with respect to each other and stabilize the angular order. Notice the occurrence of a relatively large critical value of Γ for 6 small particles. This can be explained in terms of vacancies. Between the big particles there are only 5 vacancies. When 6 small particles are added to the system, two small particles have to occupy the same vacancy (see inset of fig. 1(g)). This distorts the triangular structure and reduces the angular order, leading to a smaller angular melting temperature. If one increases the number of small particles further, the angular stabilization is restored. One can conclude that on average small particles stabilize the angular order, but the increase in angular melting temperature with respect to a cluster without small particles depends on the positioning of the small particles in the vacancies.

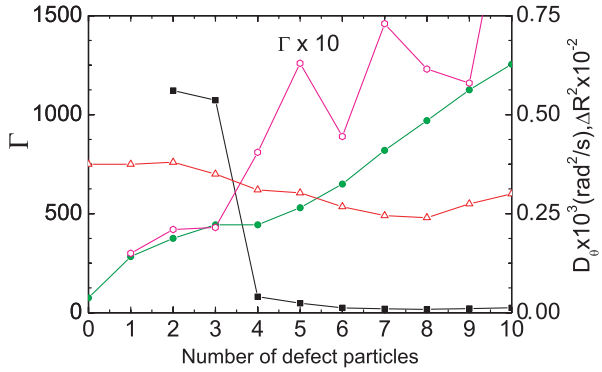

Fig. 3 – (Color online) The same as fig. 2 but now for a cluster consisting of 17 big particles.

Adding small particles does not only influence the angular melting temperature, but also the height of the plateau in the angular diffusion coefficient (shown by the (red online) triangles in fig. 2 at $\Gamma = 20$). The height of the plateau indicates how fast the shells are rotating with respect to each other. There exists an optimum number of small particles for this angular stabilization (corresponding to a minimum in this curve), which in this case is obtained for $N_S = 8$ at which the relative angular diffusion coefficient is reduced with a factor of two with respect to a system without small particles. Note also that the small dip in the relative angular diffusion coefficient for the system without small particles around $\Gamma \approx 8$ is a sign of the re-entrant behavior as studied before in ref. [10] and observed in the experiment of Bubeck *et al.* [16].

Next, we examine how these angular melting properties are modified for the non-magic cluster with 17 big particles (see right column in figs. 1 and 3). Without small particles, the relative angular order is lost at much smaller temperatures than for a magic-number configuration. Adding one small particle does not affect this melting temperature substantially for this particular system, as it will sit in the center of the cluster. However, adding more than three small particles has an even stronger influence on the melting temperature for angular melting (shown by the black squares in fig. 3) in comparison with the magic-number configuration. Again we found an optimum number of small particles for angular stabilization, which in this case also occurs for 8 small particles (see the minimum in the curve with red online triangles in fig. 3).

Radial melting. In order to describe the melting in the radial direction we calculated ΔR^2 as a function of Γ. The ΔR^2 of the big particles in the binary cluster is shown by the black squares in fig. 1. Notice that the radial melting of the big particles sets in around $\Gamma = 10$ which is independent of the number of small particles. In the limit of Γ to zero, ΔR^2 approaches $N_B/72$, which is exactly the theoretical limit for the ΔR^2 of a system of completely uncorrelated particles in a cavity with hard walls. Notice that the ΔR^2 curve of the big particles in fig. 1, exibits an increase of the inclination around $\Gamma = 10$–20 as a function of the number of small particles. To analyze this further, we show in figs. 2 and 3 the ΔR^2 of the big particles at $\Gamma = 20$ as a function of the number of small particles (green online dots) for 16 and 17 big particles, respectively. This ΔR^2 curve shows a linear increase which can be understood as follows: as the angular motion of the big particles is tempered by the small particles, most of the kinetic energy of the particles is directed into the radial direction. Summarizing, we can conclude that the radial melting temperature of the big particles is

independent of the number of small particles, but that the thermal fluctuations of the angular motion of the big particles is compensated by an increase of ΔR^2.

Comparing the ΔR^2 of the big particles with the ΔR^2 of the small particles (the red online dotted curves in fig. 1) it is seen that the radial melting of the small particles sets in at a smaller temperature than the radial melting of the big particles. This confirms the experimental observation [12] that the small particles become delocalized at a larger value of the coupling constant than the big particles. From the ΔR^2 of the small particles we notice that the radial melting of the small particles depends on the number of small particles. Figures 2 and 3 (pink online pentagons) show the critical Γ value where ΔR^2 becomes larger than 0.01 as a function of the number of small particles for a 16 and 17 particle system, respectively. The ΔR^2 curves show that the radial melting temperature increases as a function of the number of small particles. This is a consequence of the induced distortion of the triangular lattice by the small particles which is proportional to the number of small particles. The influence of this distortion is clearly visible in the ΔR^2 curve (pink online pentagons in fig. 2), just as for the angular melting temperature (black squares). For 6 small particles, at least 2 particles have to occupy a single vacancy which distorts significantly the triangular lattice of the big particles in comparison to the occupancy of only 1 small particle per vacancy. This leads also to a weaker pinning of the small particles and consequently a smaller melting temperature (*i.e.* a larger critical coupling constant). Since the interaction energy of the small particles (with charge $= q_0/8$) is less than the interaction energy of the big particles, we can expect that the critical coupling constant at which the small particles melt is between 8 times (for 1 small particle in the cluster) and 64 times (in the limit that the interaction is completely dominated by small particles) the critical coupling constant for the big particles. One can verify in fig. 1 that this is indeed the case.

An unusual behavior is found for the radial melting behavior of the small particles which is found not to occur in a single step. The ΔR^2 (red online dotted curves in fig. 1 for 16 and 17 big particles) increases suddenly at a specific Γ value. However, it does not reach its maximum value immediately. This means that the small particles at this temperature do not move freely throughout the system, but hop between the vacancies. By further decreasing Γ we even observe a decrease in the ΔR^2 before it reaches the theoretical limit of $N_B/72$, in which case the small particles move uncorrelated through the system. In contrast to the mono dispersive cluster where only an angular re-entrant behavior was observed [10], we find here a *new re-entrant behavior* but now in the radial melting of the small particles. This re-entrant melting occurs exactly at the Γ value where the relative angular diffusion coefficient increases strongly. When at large Γ the small particles temper the relative angular motion of the shells, we notice now that for smaller Γ values it is the complete angular melting which restricts on its turn the radial motion of the small particles.

Conclusion. – In conclusion, we investigated the melting behavior of a classical two-dimensional binary cluster. We showed that defect particles in such a binary cluster stabilize the angular order of the cluster. An optimum value for the number of small particles was found for this increased angular stabilization. This tempering of the angular motion of the big particles is compensated by an increase of the radial motion of the big particles. The melting process in a binary cluster takes place in several steps where first the small particles and then the big particles become delocalized with increasing temperature. Due to the radial diffusion of the small particles, the relative intershell rotation of the big particles is reduced with respect to a system without small particles. Further, with an increase of temperature, the diffusion of the big particles switches on that leads to the stabilization of the radial motion of the small particles and a re-entrant behavior of the small particles occurs.

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