Melting of two dimensional (2D) clusters of classical particles is studied using Brownian dynamics and Langevin molecular dynamics simulations. The particles are confined by a circular hard wall or a parabolic external potential and interact through a dipole or a screened Coulomb potential. We found that with decreasing strength of the inter-particle interaction clusters with short-range inter-particle interaction which are confined by a hard wall exhibit a re-entrant behavior in its orientational order.

The structural and dynamical properties of small classical two-dimensional (2D) clusters have been the subject of recent experimental studies and Monte-Carlo and molecular dynamics simulations. It was found earlier that the particles are arranged in shells and that melting of finite clusters is a two step process. With increasing temperature inter-shell motion develops and the system loses angular order. Consecutively radial diffusion switches on and destroys the shell structure of the cluster. The spectrum of such clusters was obtained in Refs. for different number of particles. The derived minimal frequencies and the corresponding energy barriers showed that ‘non-close packed’ clusters are unstable against inter-shell rotation. High symmetry clusters (i.e. the so-called magic number clusters) have energy barriers for inter-shell motion which are several orders of magnitude larger than those for ‘non-close packed’ clusters.

Recently, Bubeck et al. observed re-entrant melting in two dimensional (2D) colloidal clusters. The clusters consist of paramagnetic colloidal spheres which were confined in a circular hard wall vessel. The external magnetic field induces a magnetic moment \( \vec{M} \) in the particles and they interact through a dipole potential \( V(\vec{r}_i, \vec{r}_j) = \mu_0 M^2 / 4 \pi r_{ij}^3 \), where \( \mu_0 \) is the magnetic permeability, and \( r_{ij} \) the interparticle distance. The coupling parameter, which is the inter-particle interaction energy measured in units of the particle kinetic energy \( \Gamma = V/k_B T \), characterizes the order of the system. It decreases by lowering the external magnetic field. In Ref. it was found that with decreasing \( \Gamma \), first inter-shell rotation appears which destroys the angular order of the cluster. Further decreasing the parameter \( \Gamma \) the system unexpectantly regained angular order within a narrow range of \( \Gamma \) and then melts when \( \Gamma \) is further decreased.

It was suggested that the observed re-entrant melting behavior is due to the increasing role of the radial particle fluctuations which is very similar to an earlier investigation of laser induced melting of 2D colloidal crystals.

Earlier theoretical work on parabolic confined clusters did not find such a re-entrant behavior which suggests that the shape of the confinement potential may be very important. Another difference is that in the experimental system the particle motion is strongly damped because the colloidal particles move in water. In the present paper we investigate the mechanism for the re-entrant behavior and address the specific role played by the type of confinement (i.e. hard wall versus parabolic) and of the functional form of the inter-particle interaction (short range versus long range) on the melting of the clusters.

In our model the particles are confined by a circular hard wall potential \( (V_p = 0 \text{ for } r \leq R \text{ and } V_p = \infty \text{ at } r > R) \) or by a parabolic potential \( V_p = \alpha r^2 \). The particles interact through a dipole potential \( V(\vec{r}_i, \vec{r}_j) = q^2 / | \vec{r}_i - \vec{r}_j |^3 \), where \( q^2 = \mu_0 M^2 / 4 \pi \), or through a screened Coulomb potential \( V(\vec{r}_i, \vec{r}_j) = (q^2 / | \vec{r}_i - \vec{r}_j |) \exp(-\kappa | \vec{r}_i - \vec{r}_j |) \), with \( q \) the ‘particle charge’, \( \vec{r}_i \) is the coordinate of the \( i^{\text{th}} \) particle, and \( 1/\kappa \) is the screening length where \( \kappa = 0 \) for a Coulomb cluster and we took \( \kappa = 2/a_0 \) for the screened Coulomb cluster, where \( a_0 \) is the mean inter-particle distance. For given type of inter-particle interaction and external confinement, only two parameters characterize the order of the system: the number of particles \( N \) and the coupling parameter \( \Gamma \). We define the characteristic energy of inter-particle interaction for dipole clusters as \( E_0 = q^2 / a_0^3 \) and \( E_0 = q^2 / a_0^2 \) for screened Coulomb clusters, where \( a_0 = 2R/N^{1/2} \) for the hard wall and \( a_0 = q^2/5 \alpha^{-1/5} \) for parabolic confinement.

In the present calculation we define the coupling parameter as \( \Gamma = q^2 / a_0^3 k_B T \) for dipole clusters and \( \Gamma = (q^2 / a_0 \kappa k_B T) \exp(-\alpha a_0) \) for screened Coulomb clusters. In a different dimensionless parameter \( \Gamma \) was introduced, where \( V \) was taken to be the sum over all pairs of particles. Our coupling parameter \( \Gamma \) is a factor 2.2447 smaller than the one of for \( N = 29 \).

The ratio of the particle velocity relaxation time versus the particle position relaxation time is very small due to the viscosity of water and therefore the motion of the particles is diffusive. In our simulations we will neglect hydrodynamic interactions. Following we rewrite the stochastic Langevin equations of motion for the position of the particles as the equations of motion for Brownian
where $D_0$ is the self-diffusion coefficient, $m$ the particle mass, and $\vec{F}_L$ 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 $\Delta t \leq 10^{-4}/(nD_0)$, where $n = N/(\pi R^2)$ is the particle density and $\Delta t$ was varied within a range $(0.02 \div 0.05)$ sec. The radius of the circular vessel $R = 36 \mu m$ and the self-diffusion coefficient $D_0 = 0.35 \mu m^2/s$ are taken from the experiment. Following Ref. we consider dipole clusters consisting of $N = 29, 30, 34$ particles which have different types of packing. In the ordered state the systems of $N = 29, 30$ particles are arranged in a triangular ‘closed packed’ structure having, respectively, the shell structure (3:9:17) and (3:9:18) and ground-state energy $E = 2.2447 E_0$ and $E = 2.2798 E_0$. The cluster with $N = 34$ particles (4:11:19) $E = 2.4198 E_0$ has a non-close packed structure.

We find first the ground-state configuration using the Monte-Carlo (MC) technique. Our results for the minimal energy configuration coincides exactly with the energy found in for Coulomb clusters and in for dipole clusters with parabolic confinement. In the experiment the system was first equilibrated and after that the particle trajectories were recorded during 30 minutes. In the simulation we equilibrated the system for about $(5 \cdot 10^5 \div 10^6)$ MC steps after which we started with the statistical averaging over time of the different observables. To obtain reliable results with small statistical error we follow the particle trajectories typically during $10^7$ time steps.

We calculated the time dependence of the mean angular displacement of the particles in a specific shell $\theta(t) = \sum_{i=1}^{N} (\theta_i(t) - \theta_i(0))/N$, where $\theta_i(t)$ is the angular position of the $i$th particle and $N$ is the number of particles in a shell. In Fig. 1 the angular displacements of the particles in the first shell (the most inner) and the second shell are given as function of time for the cluster of $N = 29$ particles. The angular motion in the third shell is very small because its motion is hindered by the hard wall. Notice that both the first (thick curve) and the second (thin curve) shells take part in the angular motion, but the former rotation is more prominent. The inter-shell motion has no preferential direction and with time it can be either a clock wise or a counter clock wise rotation. With decreasing coupling parameter $\Gamma$ inter-shell rotation becomes more pronounced.

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

$$D_\theta = (\langle \Delta \theta(t)^2 \rangle - \langle \Delta \theta(t) \rangle^2)/t,$$

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 $\Delta \theta(t) = \theta^1(t) - \theta^2(t)$. The radial diffusion coefficient is

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

which is a measure of the radial order in the system.

In Fig. 2 the angular and radial diffusion coefficients are shown for three different dipole clusters with hard wall confinement subjected to the same conditions as in the experiment. For the cluster with $N = 29$ particles the angular diffusion (solid dots in Fig. 2(a)) monotonically increases with decreasing coupling parameter up to $\Gamma \sim 30$ which is a manifestation of angular melting. In the interval $\Gamma = 10 \div 30$ the inter-shell diffusion remains practically constant, and with further decreasing $\Gamma$ it is reduced to about a 20% smaller value. In the latter region the radial diffusion coefficient starts to rise (open dots in Fig. 2(a)), but the cluster retains its shell structure. In the range $3 < \Gamma < 8$ the cluster oscillates between the ground state (3:9:17) and the metastable state (4:8:17) which leads to a reduction of the angular fluctuations. Further decreasing the coupling to $\Gamma \approx 5$ both $D_\theta$ and $\Delta R^2$ rises quickly, indicating the onset of melting. A similar qualitative behavior was observed for the dipole cluster with $N = 30$ particles (see Fig. 2(b)). In the non-close-packed cluster with $N = 34$ intershell rotation occurs over all $\Gamma$’s considered in the experiment (see Fig. 2(c)) and no clear regaining of angular order is found in the region $3 < \Gamma < 8$.

In order to obtain further insight into this re-entrant behavior we investigated the conditions under which this novel effect can be observed. Therefore, we varied the following parameters: 1) the viscosity of the medium the particles are moving in; 2) the way of decreasing the coupling of the system (i.e. temperature change versus inter-particle interaction strength change); 3) the range of the inter-particle interaction; and 4) the form of the confinement potential.

To study the melting behavior of the cluster under condition of low viscosity with hard wall confinement we performed Langevin molecular dynamics (MD) simulations. The Langevin equations for the system of $N$ interacting particles are

$$\frac{d^2 \vec{r}_i}{dt^2} = -\nu \frac{d\vec{r}_i}{dt} + \vec{F}_i + \vec{F}_L/m,$$

where $\nu = D_0 m/k_B T$ is the friction and $\vec{F}_i$ the force from the inter-particle interaction. As an example, we consider $N = 30$ dipole particles moving in a medium with a viscosity which is $10^4$ times smaller than the one of water. Such a low viscosity corresponds to the situation of colloidal particles moving in a gas with pressure 1 Pa. In Fig. 3 the angular diffusion coefficient (solid circles) is plotted as function of $\Gamma$. Note that now $D_\theta$ is about
a factor $10^4$ larger as compared to previous case (see Fig. 2(b)). It is clear that changing viscosity does not destroy the re-entrant like behavior. In fact changing viscosity will not alter the statistical properties of the system but will only change the time scale for relaxation to equilibrium.

The coupling ($\Gamma$) of the system can be varied in two different ways. One can decrease the inter-particle interaction as was done in the experiment \cite{3} or increase the temperature of the system in order to induce melting. The latter approach was used for the $N = 30$ cluster and the angular diffusion constant is shown in Fig. 3 (open circles). The inter-particle interaction was chosen equal to the previous one at $\Gamma = 300$ for $T = 300K$. By heating the system no re-entrant melting behavior is observed and $D_\theta$ increases monotonically with increasing temperature $T \sim 1/\Gamma$. Thus re-entrant behavior is only found when the coupling of the system is decreased by changing the inter-particle interaction strength at fixed $T$. The reason for this unexpected behavior is that by increasing temperature the self-diffusion constant, $D_0 = k_B T/\nu m$, increases which, because $D_\theta \sim D_0$, implies that the solid dot results in Fig. 3 have to be multiplied with $T \sim 1/\Gamma$, and the resulting curve (open dots) does not exhibit a local minimum. The numerical results for the dimensionless variables (e.g. $D_\theta/D_0$) depend only on $\Gamma$ (and $N$, confinement and inter-particle interaction) but when converting them into physical variables $T, \nu, m$ enters.

Next we investigated whether the type of inter-particle interaction influences the occurrence of re-entrant behavior. We consider a cluster with long range Coulomb interaction ($N = 37$ (3:9:25) having the same internal structure as the $N = 30$ dipole cluster) with hard wall confinement using Brownian dynamics simulations. Langevin molecular dynamics simulations were carried out in the case of small viscosity. We found that only clusters with short range inter-particle interaction and confined by a hard wall well exhibit angular freezing before melting, irrespective of the value of viscosity. But it is essential that the coupling of the system is reduced by decreasing the inter-particle interaction at constant temperature as was done in the experiment \cite{3}. In the other cases, either of Coulomb clusters or with parabolic confinement the system shows the usual two step melting behavior without any re-entrance.

We showed that re-entrant behavior is a consequence of the interplay between angular order and radial oscillations where an increase of the radial fluctuations is able to induce angular order in clusters with magic number. With decreasing $\Gamma$, first angular motion sets in, because it is governed by the lowest energy barriers. Further increasing $\Gamma$ leads to an increase of the radial motion/fluctuations which hinder the angular motion. The latter prevents angular motion in case of hard wall confinement. But for parabolic confinement the average inter-particle distance (see Fig. 5) decreases which results in an equal scaling of the energy barriers for inter-shell and intra-shell motion. This contrasts with the hard wall confinement case where the inter-particle distances are unaltered and the energy barrier for inter-shell jumps decreases leading to an increase of the radial fluctuations and the inter-shell jumps. Thus anharmonic effects are essential for the occurrence of this re-entrant behavior. Anharmonicity is enhanced in systems with hard wall confinement and for short-range inter-particle interaction.

Last we study the effect of the shape of the confinement potential and consider the melting behavior of a cluster with short range inter-particle interaction in a parabolic well. We choose the $N = 25$ dipole cluster (3:9:13). Fig. 5 shows the angular diffusion and the radius of the cluster as function of $\Gamma$. $D_\theta$ clearly does not exhibit a local minimum, it rises uniformly with decreasing $\Gamma$, and melting occurs for $\Gamma \approx 5$, as in the case of hard wall confinement. The radius of the cluster $R$ and the mean inter-particle distance changes proportionally to $\Gamma^{1/2}$.

In conclusion, we studied the melting transition of 2D clusters with dipole and screened Coulomb type of interaction confined by a hard wall or a parabolic external potential using Brownian dynamics simulations. Langevin molecular dynamics simulations were carried out in the case of small viscosity. We found that only clusters with short range inter-particle interaction and confined by a hard wall well exhibit angular freezing before melting, irrespective of the value of viscosity. But it is essential that the coupling of the system is reduced by decreasing the inter-particle interaction at constant temperature as was done in the experiment \cite{3}. In the other cases, either of Coulomb clusters or with parabolic confinement the system shows the usual two step melting behavior without any re-entrance.

One of us (FMP) thanks C. Bechinger for fruitful discussions. This work is supported by the Flemish Science Foundation (FWO-Vl), IUAP-IV and the Russian Foundation for Fundamental Investigation 96–023–9134a. One of us (FMP) is a Researcher Director with FWO-Vl and I.V.S and V.A.S are supported by a DWTC–fellowship.

\begin{thebibliography}{99}
\bibitem{1} W.-T. Juan, Z.-H. Huang, J.-W. Hsu, Y.-J. Lai, and Lin I, Phys. Rev. E \textbf{58}, R6947 (1998).
\bibitem{2} D.J. Wineland, J. C. Bergquist, W.M. Itano, J.J. Bollinger, and C.H. Manney, Phys. Rev. Lett. \textbf{59}, 2935 (1987).
\bibitem{3} R. Bubeck, C. Bechinger, S. Neser, and P. Leiderer, Phys.
\end{thebibliography}
[4] Yu.E. Lozovik and V.A. Mandelshtam, Phys. Lett. A 145, 269 (1990).
[5] V.M. Bedanov and F.M. Peeters, Phys. Rev. B 49, 2667 (1994).
[6] V.A. Schweigert and F.M. Peeters, Phys. Rev. B 51, 7700 (1995).
[7] I.V. Schweigert, V.A. Schweigert, and F.M. Peeters, Phys. Rev. B 54, 7700 (1995).
[8] V.A. Schweigert and F.M. Peeters, J. Phys.: Condens. Matter 10, 2417 (1998).
[9] A.I. Belousov and Yu.E. Lozovik, cond-mat 9806108.
[10] L. Cândido, J.-P. Rino, N. Studart, and F.M. Peeters, J. Phys.: Condens. Matter 10, 11627-11644 (1998).
[11] J. Chakrabarti, H.R. Krishnamurthy, A.K. Sood, and S. Sengupta, Phys. Rev. Lett. 75, 2232 (1995).
[12] Q.-H. Wei, C. Bechinger, D. Rudhardt, and P. Leiderer, Phys. Rev. Lett. 81, 2606 (1998).
[13] D.L. Ermak and J.A. McCammon, J. Chem Phys. 69, 1352 (1978).

FIGURES

FIG. 1. The angular displacement of the particles on the first (thick curves) and second (thin curves) shell for a cluster with \( N = 29 \) particles for different values of the coupling parameter: (a) \( \Gamma = 150 \), (b) \( \Gamma = 46 \), (c) \( \Gamma = 10 \), and (d) \( \Gamma = 3 \).

FIG. 2. The angular diffusion \( D_\theta \) (solid circles) and the radial diffusion \( (\Delta R^2) \) (open circles) coefficients as function of \( \Gamma \) for clusters with (a) \( N = 29 \), (b) \( N = 30 \), and (c) \( N = 34 \) particles.

FIG. 3. The angular diffusion coefficients as a function of the strength of the inter-particle interaction at constant temperature (solid circles) and as function of temperature (\( \Gamma \sim 1/T \)) for fixed inter-particle interaction strength (open circles) for a dipole cluster with \( N = 30 \) in the case of small viscosity.

FIG. 4. The angular (solid circles) and radial diffusion (open circles) coefficients as function of \( \Gamma \) for: (a) the Coulomb cluster with \( N = 37 \) particles, and (b) the screened Coulomb cluster with \( N = 30 \) particles confined by a hard wall potential.

FIG. 5. The angular diffusion coefficient (solid circles) and radius of the cluster (open triangles) as function of \( \Gamma \) for a \( N = 25 \) dipole cluster in a parabolic well.
Fig. 2(a)
Fig. 2(b)
Fig. 2(c)

\[ \Delta R^2 \]

\[ D \theta \times 10^3 \text{ (rad}^2/s) \]

\[ \Gamma \]

\[ N=34 \]
Fig. 3

$D_\theta$ (rad²/s)

$\theta_x 10^{-1}$ (rad²/s)

$\Gamma$

$N=30$
Figure 4(a) shows a graph plotting $\Delta R^2$ against $\Gamma$, with $N=37$. The data points are marked with filled circles and open circles, and error bars are indicated. The graph also shows $D \times 10^3 (\text{rad}^2/\text{s})$ on the y-axis.
Fig. 4(b)

N = 30

\[ D_\theta \times 10^3 \text{ (rad}^2/\text{s}) \]

\[ \Delta R^2 \]
Fig. 5

N = 25

$R/a_0$

$D_{\theta} \times 10^3$ (rad$^2$/s)

$\Gamma$

Fig. 5