Dynamics of topological defects and the effects of the cooling rate on finite size two-dimensional screened Coulomb clusters

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Abstract. - The formation of dislocations, disclinations and their dynamics is central to our understanding of crystalline materials. Here, the dynamics of these topological defects in two-dimensional (2D) clusters of charged classical particles interacting through a screened Coulomb potential is investigated through the Molecular Dynamics (MD) simulation technique. The particles are confined by a harmonic potential and coupled **to** an Anderson heat reservoir. We investigate cooling rate effects on the defect dynamics by decreasing the temperature of the heat reservoir linear in time. We found that: i) the mobility of **the** defects strongly depends on the number of nearest neighbors and the nature of those defects, ii) geometrically induced defects have different dynamics than other defects because of spontaneous pinning of the defects at the corners of the hexagon, and iii) if the cooling speed is large enough, the system ends up in a non-equilibrium state and a glass like structure is formed.

Introduction. – When a liquid is cooled, it can solidify in two very different ways. It can form an ordered crystal or become a glass, depending on the cooling rate. For slow cooling rates, the system will crystallize in a metastable state containing defects close to the ground state. A liquid undergoes a glass transition when crystallization is avoided during the cooling process. Or in other words, when the cooling rate exceeds the relaxation time scale of the system, the system will be out of equilibrium and it undergoes a glass transition.

An important aspect in the formation of crystals is the dynamics of defects during the cooling process. The phenomenology of crystals and glass formation has been known for decades [2, 3], but we are still far from understanding the relevant features of molecular motion. Experiments have not allowed us to directly measure how a molecule moves relatively to a particular neighbor in a glass or to observe which local structures are prone to reorganization. This is the reason why one started studying two dimensional systems with charged particles like e.g. colloids [4] and dusty plasma's [5] which display similar phase behaviour 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 [6].

In a recent study of a 3D system consisting of hard spheres [7] dynamical heterogeneities were found. Shortly after this experiment a new experiment showed [8] that fast moving particles were organized in clusters. The behaviour of the formed clusters indicated very inhomogeneous relaxations. This correlated motion can play a critical role in the dynamics of the sample near the glass transition, and its consequences must be incorporated in any theoretical treatment. In this work we want to investigate if similar effects that depend on the cooling rate are present in finite 2D systems. One of the questions we want to answer is: "can we find the analogue of a glass transition in 2D *finite* systems?".

In contrast to theoretical work, where it is possible to find the ground state for such a finite system with a limited number of particles, experimentalists always find a metastable state of the system when cooling and annealing the system to a very low temperature. Despite this limitation, a very good agreement between experiment and theory was found for the dynamical properties like melting [1, 9] and reentrant behaviour [10–12], and for the static properties like shell structure formation [9]. It was also found that melting of a large (i.e. $N < 150$) 2D cluster was initiated by topological defects organized at the six corners of a hexagon which were called geometrically

induced defects [13].

But, important questions regarding the dynamics of defects and cooling rate effects in these finite 2D systems remained unanswered. In this paper we investigate the importance of defect dynamics in finite two dimensional systems during the cooling process and on the formation of crystals or glasses by measuring single defect diffusion and the potential energy of the system. In contrast to previous theoretical studies in which the melting properties of two-dimensional Coulomb clusters were studied [16], we investigate here the effects of the cooling rate on the defect dynamics. Up to now, only one experimental study of defect dynamics was reported for a 3D spherical colloidal crystal [14] where it was found that the defects assemble into scars.

In this paper we will first show the different diffusion mechanisms that are active and the effect of a boundary in a finite 2D system during the formation of crystals, i.e. by slowly cooling the system. Further we show that if the cooling rate is increased beyond the relaxation times of the system a glass-like structure is formed.

Model system. – We study a 2D model system of N equally charged particles and confined in a parabolic potential interacting through a repulsive screened Coulomb potential:

$$V = \sum_{i=1}^{N} \frac{1}{2} m\omega_0^2 r_i^2 + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} q^2 e^{-\kappa|\vec{r}_i - \vec{r}_j|}/|\vec{r}_i - \vec{r}_j|, \quad (1)$$

where m is the mass of the particle, $r_i = (x_i, y_i)$ is the vector position of the ith particle, and κ the inverse screening length. If we take as units for length $r' = (q^2/\gamma)^{1/3}$, for energy $E' = \gamma r'^2$ and for time $t' = \sqrt{2}/\omega_0$ with $\gamma = m\omega_0^2/2$, the potential energy can be expressed in dimensionless form:

$$V = \sum_{i=1}^{N} r_i^2 + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} e^{-\kappa|\vec{r}_i - \vec{r}_j|}/|\vec{r}_i - \vec{r}_j|. \quad (2)$$

All the results are given in dimensionless units. For our numerical study we take the dimensionless inverse screening length $\kappa = 5$.

We simulate the cooling of the system by performing molecular dynamics simulations in which the system is coupled to a heat bath as was proposed by Andersen [17]. We decrease the temperature $T(t)$ of the heat reservoir linearly in time, i.e. $T(t) = T_i - \gamma t$ with γ the cooling rate of the system, t the time, and T_i the initial temperature. The equation of motion is integrated with the velocity form of the Verlet algorithm with time step $\Delta t = 10^{-3} - 10^{-4}$. The thermostat is a stochastic collision procedure which randomly substitutes the velocities of the particles according to a Boltzmann distribution that corresponds to the temperature of the heat bath. To improve the statistics we start from 50 different uncorrelated initial positions and average all the results over these 50 independent runs.

The cooling of the system is continued until the temperature of the heat bath is zero. The final obtained configuration is further relaxed using the Newton optimization technique [16]. The Newton optimization method is similar to molecular dynamics simulations at zero temperature but with increased efficiency.

A defect is defined as a particle which does not have six nearest neighbours. The defects in the system are characterized in different ways. We call a particle with 5 nearest neighbours as a negative or a 5-fold coordinated defect (with topological charge -1) and a particle with 7 nearest neighbours as a positive or 7-fold coordinated defect (with topological charge +1). Furthermore, defects can arrange themselves as dislocations or disclinations. A dislocation consists of an equal number of tightly bound positive and negative defects with a zero total topological charge, a disclination is a **single defect with 5 or 7 nearest neighbors or by extension an array of defects with a total net charge**. The number of disclinations in a finite **size circular** two dimensional cluster is determined by Euler's theorem and the total topological charge is equal to -6. These six disclinations can be considered as geometrically induced defects. The other defects will be called randomly induced defects.

The simulation. – In order to analyse single defect diffusion, a new variable was constructed, as was proposed by S. Ratynskaia *et al.* [15]. At every time step the cumulative sum $\xi_j = \sum_{i=1}^{j} \delta\xi_i$ of the azimuthal position displacements is calculated for each particle, with $\delta\xi_i = r_i \delta\varphi_i$. Here r_i is the distance from the center of the cluster at time $i\delta t$, and $\delta\varphi_i$ is the increment in the azimuthal angle from time $(i-1)\delta t$ to $i\delta t$. The choice of the quantity ξ_j is motivated by the fact that the azimuthal displacement is not limited by the boundary in contrast to the radial displacement. A measure which characterizes the azimuthal diffusion of each particle is now given by $\Delta\xi_j(\tau) = \xi_{j+\tau/\delta t} - \xi_j$ over the time lag $\tau = 0.1$, which we call the azimuthal diffusion parameter. In the calculation of the azimuthal diffusion parameter we only take into account the inner particles of the cluster. The azimuthal diffusion of the defects is obtained by averaging this azimuthal diffusion parameter over particles with the same number of nearest neighbours.

Defect dynamics during slow cooling. – A lot of research in the past was directed to the study of low dimensional crystals. However very little is known about the formation of crystals and the defect dynamics during the cooling process. Here we investigate how defects are diffusing and relaxing during the cooling process.

As reference system we choose a 200 particle system which is large enough to see already semi-bulk effects, but small enough to obtain results within an acceptable time period. To be sure that all particles are initially uncorrelated at the beginning of the simulation we started at a sufficiently high temperature $T = 0.1$. A relatively simple

quantity to study during the cooling process is the average proportion of 7-fold and 5-fold coordinated defects in the system. We show in Fig. 1 the defect density as function of temperature for a cooling rate of $\gamma = 10^{-4}$. The red **dashed** line presents the density of the 7-fold coordinated defects, the blue **dotted** line the 5-fold coordinated defects and the black full line the other 'neutral' particles. As expected, the number of defects decreases during the cooling process because the system tries to form a crystalline structure in order to minimize its potential energy.

How do these defects vanish in the system? A first insight is given by investigating the defect density as function of the radial position for three fixed temperatures as shown in the **density profiles** of Fig. 1. For high temperature (Fig. 1(c) - liquid phase) the number of defects is large and homogeneously distributed **throughout** the system. When cooling the system, we notice from Fig. 1(a) that beside a reduction of the defect density we also observe that the defects migrate from the center of the system to the outer shells. The signature of crystallization is seen as indicated by the oscillations in the density profile curves as function of the radial coordinate indicating shell formation. Note from Fig. 1(c) that the onset of the crystallization process takes place in the center. This agrees with the results in Ref. [1] where it was shown that in a 2D system consisting of a finite number of repelling particles which are held together by a circular harmonic potential, the cluster patterns are determined by the need to balance the tendency to form a triangular lattice against the formation of a compact circular shape. These defects were called *geometrically induced defects* and are located at the six corners of a hexagon. It was shown that the melting of such a cluster is initiated by these topological defects. In our case we cool the system to zero temperature from an initial temperature $T = 0.1$. First the system crystalizes in the center and ends with a symmetry breaking at the six corners of a hexagon. The existence of geometrically induced defects is clearly visible in Fig. 1 where the density curve of the 5-fold coordinated defects is almost an equidistance of the 7-fold coordinated defect density curve. By analyzing this more closely we found that on average there are six 5-fold coordinated defects more than 7-fold coordinated defects as should be according to Euler's theorem.

Now we will investigate the possible different defect dynamics and the mechanisms that lead to an annihilation of defects. Therefore we analysed the azimuthal diffusion of the different kind of defects. In Fig. 2(a) the azimuthal diffusion of the defects for a system consisting of 200 particles is plotted. We can clearly distinguish three phases marked by the vertical black dotted lines: The liquid phase (*III*) where the azimuthal diffusion of the 5-fold coordinated defects (blue line with open squares) is larger than the diffusion of the neutral particles (black line with closed squares) and the 7-fold coordinated defects (red line with triangles); the crystalized phase (*I*) where the azimuthal diffusion of the 5-fold coordinated and the 7-fold coordinated defects particles are equal, and the transition phase (*II*) where the **crystalisation** of the neutral particles starts and where the diffusion of the 7-fold coordinated particles changes its behaviour.

In order to understand the differences between the diffusion curves for neutral, 5-fold and 7-fold coordinated particles in the liquid region we have to consider two properties, first the number of nearest neighbors and secondly the preferential triangular structure. If we look at the nearest neighbours only, we expect a larger diffusion for the low coordinated particles because they have by definition less nearest neighbours and are consequently less confined by there neighbouring particles. However if we look at region *III* we see that the diffusion of the 7-fold coordinated defects is only slightly lower than the diffusion of the neutral particles which is unexpected. To explain this behaviour we have to take into account the distortion of the triangular lattice by the 7-fold coordinated particles which leads to a higher mobility of the particles around the distortion. We can conclude that the distortion of the lattice by the positive defects compensates the effect of a lower coordination number leading to similar diffusion properties as for neutral particles.

If we cool down the system further till region I, the geometrically induced disclinations will occupy the 6 corners of a hexagon. Those defects, which are 5-fold coordinated, will be pinned at those corners because of geometrical considerations and are less mobile than the randomly induced defects. These disclinations **will** grow by adding 5-7 fold coordinated pairs forming a chain of alternating 5-fold and 7-fold coordinated defects. As a result, in region *I* the motion of the 7-fold coordinated defects becomes coupled with the motion of the 5-fold coordinated defects and both diffusion curves become equal. Therefore the diffusion of the 7-fold coordinated defects is first decreasing (region III) and **then** increasing (region II) with decreasing temperature, which is a clear reentrant behaviour of the azimuthal diffusion of 7-fold coordinated defects. To investigate the pinning phenomenon more closely we tried to make a distinction between geometrically and randomly induced defects because we expected the geometrically induced defects to be less mobile and more stable than randomly induced defects. Therefore we **studied** the diffusion of defects in a smaller system, where the number of randomly induced defects is smaller and the geometrical defects are more predominant. In Fig. 2(b) the diffusion of defects in a system consisting of 100 particles is given. Here we found the azimuthal diffusion of the 5-fold coordinated defects indeed to be smaller than the diffusion of the 7-fold coordinated particles.

Formation of a glass. – So far we discussed the dislocation dynamics during slow cooling. Here, in this section we will show the importance of the cooling speed on the formation of crystals and glasses.

Like mentioned before the temperature of the system is decreased linear in time by decreasing the temperature of

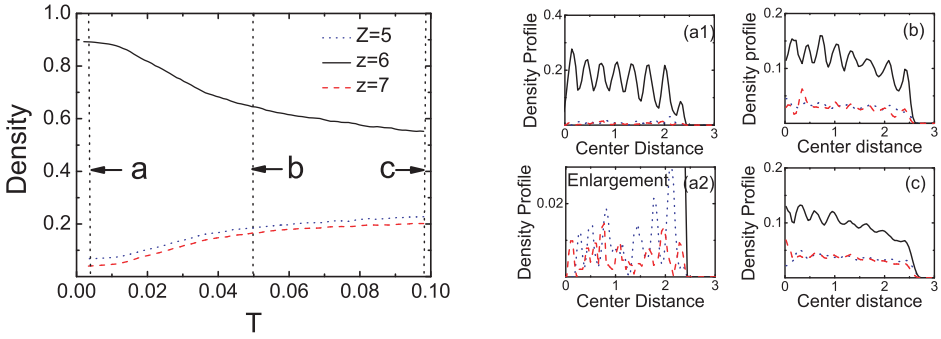

Fig. 1: (color online) Probability of finding neutral and defect particles as function of temperature for a cooling rate of $\gamma = 10^{-4}$. The red **dashed** line shows the 7-fold coordinated defects and the blue **dotted** line the 5-fold coordinated defects. The inverse screening length of interaction is $\kappa = 5$. The **figures at the right show the density profile of the z=5,6,7 coordinated particles as function of radial distance at T=0.1 (labeled with (a1) and (a2)), T=0.05 (labeled with (b)) and T=0.009 (labeled with (c)), respectively.**

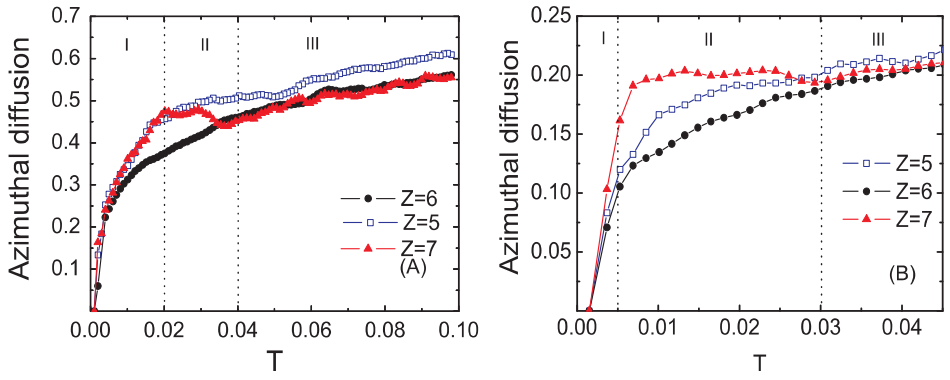

Fig. 2: (color online) (a) The azimuthal diffusion of a system consisting of 200 particles as function of temperature. The red triangles show the 7-fold coordinated defects, the blue squares the 5-fold coordinated defects and the black circles give the results of the 6-fold coordinated particles. (b) The same as (a) but now for a system consisting of 100 particles.

the heat reservoir. This heat reservoir is strongly coupled to the system so that, when the system is cooled at very high cooling rates, it will follow the temperature of the heat reservoir. (A weakly thermal coupled system results only in more noisy results because the timescale of the **internal dynamics** becomes larger than the timescale of cooling).

Often in the literature the glass transition is determined as the point where the total energy-temperature curve is bending. Because in our case the external work on the system is zero and the kinetic energy is linearly decreasing with temperature due to the strong thermal coupling, it is appropriate to look for a bend in the potential energy curve.

In Fig. 3 the potential energy as function of temperature is given for several cooling rates investigated for a 200 particle system. For decreasing cooling rate the system approaches the behaviour given by the blue dotted curve. This limit is reached when the cooling of the system is sufficiently slow such that its potential energy can attain its minimum. If a system exceeds this critical cooling rate the system will no longer be in thermodynamic equilibrium and a glass transition occurs**, or more precisely, the system is not able anymore to stay closely to a local or global minimum energy configuration**. The temperature at which a bend in the kinetic energy occurs is identified as the glass transition **temperature** (see Fig. 3(b)).

To show the influence of the cooling rate on the glass transition, Fig. 4 shows the glass transition temperature and the number of defects after cooling as function of the cooling rate. A small increase of the glass transition temperature is found but a sudden increase occurs if a critical cooling rate is reached. This behaviour is explained by the fact that for high cooling rates the system is no longer in thermodynamic equilibrium and consequently the system is no longer able to minimize its potential energy. If the cooling rate is large enough the system will reach a configuration with maximal energy and number of defects which is indicated by the red dash dot line in the potential curve in Fig. 3(b).

Conclusions. – We have performed molecular dynamics simulations of a screened Coulomb clusters in order to investigate the role of defect dynamics during the formation of crystals and the influence of the cooling rate on the formation of glasses.

Our analysis on the formation of crystals shows that defects are vanishing in the center first and are pinned at the corner of a hexagon at zero temperature. For large clusters, a clear reentrant behaviour of the azimuthal diffusion of 7-fold coordinated defects was observed. The geometrically induced defects are shown to be less mobile in comparison with the randomly induced defects.

Our analysis of the formation of glasses show a cooling rate dependency of the glass structure. A glass was formed when the cooling rate is so high that the relaxation times

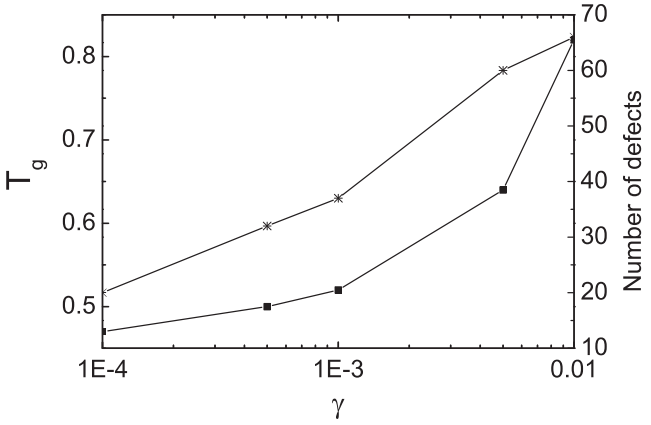

Fig. 4: Glass transition temperature (squares) and number of defects after cooling (stars) as function of the cooling rate γ

of the system at the glass transition temperature is no longer able to equilibrate the system.

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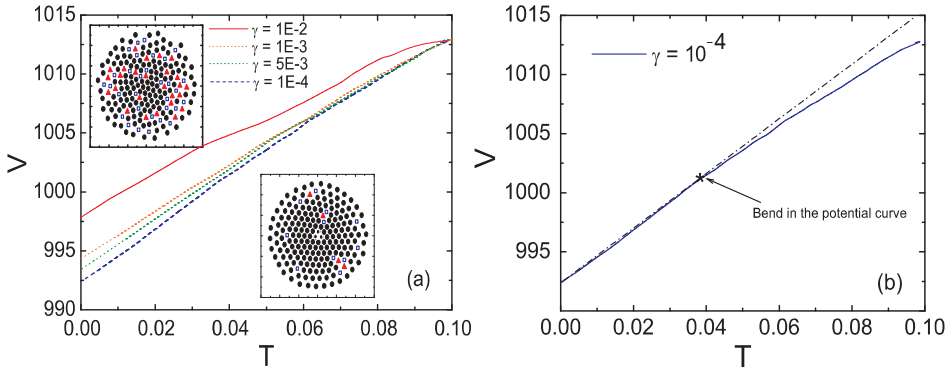

Fig. 3: (color online) (a) Potential energy of the system as function of T, temperature of the heat bath **for different cooling rates**. (b) The potential energy of the system as function of T for $\gamma = 10^{-4}$. The **dash** dotted straight **line** highlight the **knick** in the potential curve.

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