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The stable state of charge polydisperse colloids: disordered or charge ordered?

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Abstract. Charge polydisperse colloidal crystals have been recently reported to turn amorphous beyond a critical charge polydispersity (CPD). The resulting disordered (amorphous) state, due to its unusual structural properties, has been conjectured to be different from that obtained from quenching of atomic liquids and is probably a *stable* state. In order to confirm this, Monte Carlo simulations with different initial configurations are performed and properties of equilibrium states investigated. In contrast to a monodisperse system, which always evolves to a crystalline structure irrespective of the initial configuration, the charge polydisperse system with random charge distribution is found to remain disordered. On the other hand, for the same CPD an ordered crystalline state is found to remain in equilibrium when evolved from a charge-ordered initial configuration. Simulated annealing, by gradually decreasing impurity ion concentration n_i (which is equivalent to the lowering of temperature) and evolving at each n_i , is also carried out to obtain the low-temperature (ground) state. From the present investigations it is concluded that beyond a critical CPD the charge polydisperse system remains in a stable disordered state unlike atomic glasses (obtained by quenching) which are known to be metastable. Based on some common properties an analogy is made between a spin glass and the amorphous state. The stability aspects of this amorphous state and charge-ordered states are also discussed.

1. Introduction

Usually disordered atomic solids (i.e., without long-range order) consist of monodisperse atoms or molecules. If the disordered solid is obtained by quenching a liquid, it is usually known as glass [1]. A disordered state obtained by other means such as pressure-induced amorphization of crystalline solids [2, 3] or by ion implantation is called an amorphous solid [4]. The terms 'glass' and 'amorphous solid' have been extensively used interchangeably [5, 6]. The disordered (glass or amorphous) state of atomic solids is metastable as there always exists a stable crystalline state. Unlike atomic systems, particles in a colloidal suspension are not identical. The variation of size and charge from particle to particle, which can be described by a suitable distribution, can influence the structural ordering [7–9], particle diffusion [8, 9] and the thermodynamic properties [6, 7] of the suspension. In the case of hard-sphere colloids, it has been shown that there exists a critical size polydispersity beyond which the crystalline order gets disrupted [10]. In the case of charge-stabilized colloidal systems polydispersity in size as well as in charge influence the structural order. However, in the case of dilute systems (particle volume fraction $\phi \sim 10^{-3}$) the polydispersity in charge plays a dominant role in disrupting the crystalline order. Tata and Arora [9] have shown that beyond a critical charge polydispersity the crystalline order gets disrupted resulting in an amorphous state. They also obtained the phase diagram [8] of such a charge polydisperse

system by varying charge polydispersity (CPD) and impurity ion concentration n_i . Using the concept of effective hard-sphere diameter associated with each charge, the equivalence between size and charge polydisperse systems has been obtained [9, 6] and it has been argued that incompatibility of packing (i.e size-mismatch frustration) of these hard spheres in a crystalline state leads to an amorphous state. Alternatively the polydisperse system is also viewed as an n -component system with nearest-neighbour interactions being randomized [11]. Using this as a basis, a nearest-neighbour model was worked out to understand the CPD-driven crystalline to amorphous transition [11]. The structural parameters of charge polydisperse glass are found to be different from those of a conventional glass across melting [8]. In addition to this, the Monte Carlo (MC) simulations also show that for CPD values greater than the critical CPD the body-centred cubic (BCC) lattice becomes unstable and evolves into an amorphous state. The monotonic decrease of total interaction energy U_T and the increase in entropy upon increasing CPD [11] suggest a decrease in free energy. Analytical calculations carried out by Löwen *et al* [6] for charge polydisperse systems also show lowering of excess free energy. These observations led investigators to propose that the nature of the disordered state of a charge polydisperse system could be different from that obtained by quenching. Based on some of the above-mentioned results it has also been conjectured that the disordered state of a charge polydisperse system could be a stable state unlike that obtained by quenching. Löwen *et al* [6] have conjectured that a charge polydisperse system favours a charge ordering to lower the free energy, which needs to be confirmed.

In the present work, we have carried out a number of MC simulations with widely different initial configurations for monodisperse systems as well as for different values of charge polydispersities with the aim of understanding the stability of charge-ordered and disordered states of the system. Simulated annealing studies also have been carried out to find out whether a charge polydisperse system, with charges on particles being randomly distributed, favours a charge-ordered state or a disordered state. The results of these investigations are discussed. The organization of the paper is as follows.

Details of Monte Carlo simulations are given in section 2. Section 3 deals with simulation results for monodisperse and charge polydisperse colloidal systems. Section 4 presents the results of the simulation of the charge-ordered state and its stability. Section 5 describes the simulated annealing investigations. A detailed discussion of all the results along with brief conclusions are given in section 6.

2. Details of simulation

Monte Carlo simulations of an aqueous colloidal suspension of polystyrene spheres ($\phi \sim 10^{-3}$) interacting via a size-corrected screened Coulomb pair potential given by

$$U(r_{ij}) = \frac{Z_i Z_j e^2}{\epsilon} \left[\frac{4 \exp(Kd)}{(2 + Kd)^2} \right] \frac{\exp(-Kr_{ij})}{r_{ij}} \quad r_{ij} > d \quad (1)$$

are carried out using the well known Metropolis algorithm for a canonical ensemble (constant NVT where N , V and T are number of particles, volume of the MC cell and temperature respectively). d is the diameter of the particle which is taken to be 109 nm, Z_i is the charge on the i th particle, r_{ij} is the separation between particles i and j and ϵ is the dielectric constant of the water. K is the inverse Debye screening length, arising due to the counter-ion concentration $n_p Z_0$ and impurity ion concentration n_i , and is given as

$$K^2 = \frac{4\pi e^2}{\epsilon k_B T} (n_p Z_0 + n_i). \quad (2)$$

n_p is the particle concentration, Z_0 is the average charge, k_B the Boltzmann constant. Z_0 is taken to be 600 [12] and n_i is taken to be zero unless stated otherwise.

In order to simulate a charge polydisperse system, charges on the particles are taken from a symmetric rectangular distribution $P(Z)$ with mean Z_0 and width 2Δ given as

$$P(Z) = \begin{cases} (2\Delta)^{-1} & \text{for } Z_0 - \Delta \leq Z \leq Z_0 + \Delta \\ 0 & \text{otherwise.} \end{cases} \quad (3)$$

Charge polydispersity is defined as

$$\text{CPD} = (\langle Z^2 \rangle - \langle Z \rangle^2)^{1/2} / \langle Z \rangle \quad (4)$$

and is related to the width of the distribution as $\text{CPD} = \Delta / \sqrt{3} Z_0$. Angular brackets in equation (4) denote the average and $\langle Z \rangle = Z_0$. Once the charges are assigned, the charge on the particle is not changed throughout the simulation. The average charge Z_0 is kept constant throughout the simulations. All the simulations are carried out at $T = 298$ K and for $N = 432$ using periodic boundary conditions. The size L of the MC cell is chosen to correspond to $n_p = 1.33 \times 10^{12} \text{ cm}^{-3}$. The total interaction energy U_T is obtained by assuming pairwise additivity of the interaction. This is reasonable as the average interparticle separation $a_s (= n_p^{-1/3}) > K^{-1}$. MC simulations are performed with a step size of 0.5d which yielded an average value of trial acceptance ratio as 50% [13].

If the simulation parameters are close to a phase transition (e.g., melting or crystalline to amorphous transition) slowing down of the MC evolution process (the rate at which system reaches equilibrium from the initial configuration) can take place [14, 15]. In such a situation it is known that monitoring the height of the first peak of the structure factor, S_{max} , along with U_T is useful in finding out unambiguously whether the system has reached thermal equilibrium or not. Hence, S_{max} , U_T are monitored during the evolution of the system. Most of the simulations away from the transition took approximately 9×10^5 configurations to reach equilibrium, while those close to the transition took nearly 6×10^6 . A Monte Carlo step (MCS) is defined as the set of N configurations during which, on average, each particle gets a chance to move. After reaching equilibrium, the pair correlation function $g(r)$ is calculated with an interval $\Delta r = 0.1d$ using the standard method [16] and averaged over 2.1×10^5 configurations. The mean square displacement is obtained using $\langle r^2(m) \rangle = \langle (1/N) \sum_{j=1}^N [r_j(m+n) - r_j(n)]^2 \rangle$ after reaching equilibrium. In order to reduce statistical fluctuations, the mean square displacement is averaged over 50 different choices of initial frame n . In order to find out the system size effect, some of the simulations have been carried out with 250 particles and the results are found to be the same within the statistical error [9], thus suggesting that even 250 particles are sufficient. We also carried out a simulation with 431 particles and found the system to remain in BCC crystalline order. The results reported here correspond to $N = 432$. We also chose for $P(Z)$ a Gaussian distribution and performed simulations. The results are found to depend only on the magnitude of CPD and not on the nature of the distribution [15].

A charge polydisperse system with continuous polydispersity can also be divided into a pseudobinary system with charges $Z_1 < Z_0$ and $Z_2 > Z_0$ having narrower distributions $P_1(Z_1)$ and $P_2(Z_2)$ as shown in figure 1. A charge-ordered initial configuration is prepared by placing small charges from the $P_1(Z_1)$ distribution on the cation sublattice of the CsCl-type structure and large charges (Z_2) on the anion sublattice from the other distribution $P_2(Z_2)$. For the same polydispersity a random initial state is prepared by placing the charges taken randomly from the total distribution, $P(Z)$, on the BCC lattice (hereafter this state is called the random initial state). The charge order of the initial states prepared can be immediately confirmed by calculating partial correlation functions ($g_{11}(r)$, $g_{22}(r)$ and

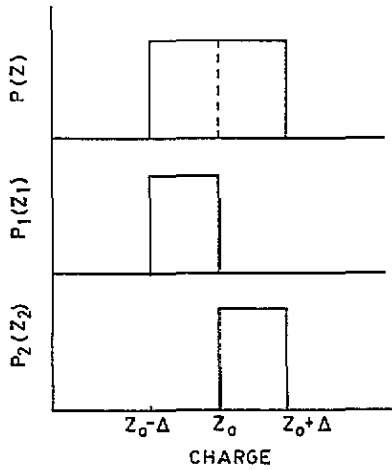


Figure 1. Schematic diagram of the charge distribution function $P(Z)$ as a function of Z . $P_1(Z_1)$ and $P_2(Z_2)$ constitute the pseudobinary charge distributions derived from $P(Z)$ and correspond to small $Z_1 < Z_0$ and large charges $Z_2 > Z_0$ respectively.

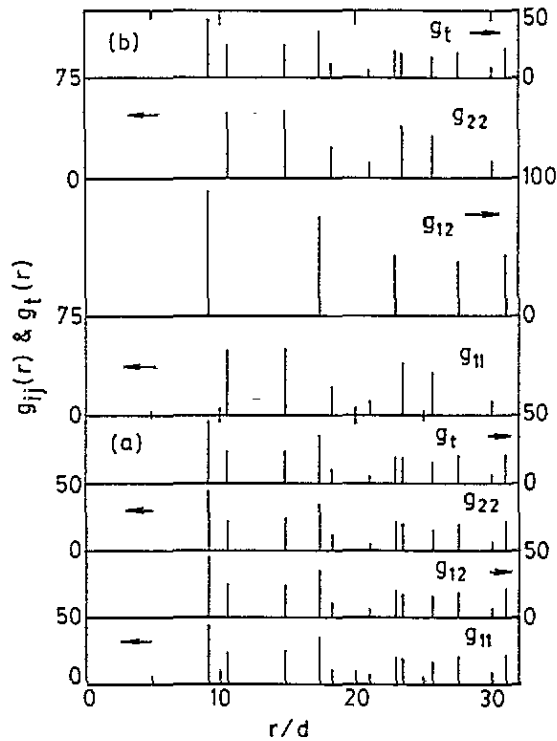


Figure 2. Partial pair correlation functions $g_{ij}(r)$ and total pair correlation function $g_t(r)$ as a function of r for (a) a BCC initial configuration with particle charges being randomly distributed and (b) a CsCl-type charge-ordered initial configuration.

$g_{12}(r)$) and the total correlation function $g_t(r)$. Here, the suffixes 1, 2 refer to small and

large charges respectively. The total correlation function $g_t(r)$ is defined as

$$g_t(r) = c_1^2 g_{11}(r) + c_2^2 g_{22}(r) + 2c_1 c_2 g_{12}(r). \quad (5)$$

Here, c_1 and c_2 refer to the concentrations of small and large charges respectively. Since the charges are divided equally between the two distributions P_1 and P_2 , the values of c_1 and c_2 become 0.5. Figure 2 shows the pair correlation functions calculated for the charge-ordered and random initial states. It is clear from figure 2 that one can very clearly characterize random and charge-ordered states from partial correlation functions. One can also notice that the $g_t(r)$ is the same for both initial states.

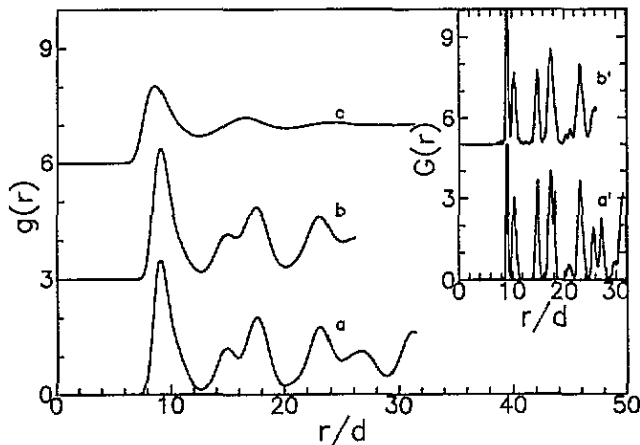


Figure 3. Pair correlation function $g(r)$ versus r for a monodisperse suspension. Curve a corresponds to the system evolved from BCC initial configuration at $n_i = 0$. Curve b corresponds to the system evolved from a liquid-like ordered initial configuration after quenching to $n_i = 0$. $g(r)$ corresponding to the initial state for curve b (liquid-like ordered suspension at $n_i = 2.6n_p Z_0$) is also shown as curve c for the sake of comparison. The inset shows the coordinate-averaged pair correlation functions $G(r)$. The curves a' and b' correspond to the same parameters as those of curves a and b . The first peak height of curve a' is 13.4 and that of curve b' is 13.6.

In order to determine the extent of charge ordering the Warren-Cowley short-range order parameter α [17] defined as

$$\alpha = 1 - \frac{f_{12}}{c_2^2 f_{11} + (c_1^2 + c_2^2) f_{12} + c_1 c_2 f_{22}} \quad (6)$$

is calculated. f_{ij} refers to the number of j atoms in the first coordination shell of atom i , and is calculated using the following equation:

$$f_{ij} = \int_0^{r_2} 4\pi n_p r^2 g_{ij}(r) dr \quad (7)$$

where r_2 is the position of the minimum after the first peak in $4\pi r^2 g_{ij}(r)$. One can immediately see that α must be -1 for a CsCl-type charge-ordered state and zero for a random initial state. Thus, during the MC evolution process, whether the charge polydisperse system favours a charge ordering or not can also be determined.

We have considered only a CsCl type and no other type (e.g. AB_n type) of charge-ordered states for the following reasons. Since the distribution given by (3) corresponds to a continuous distribution, the distributions P_1 , P_2 constructed from $P(Z)$ are only

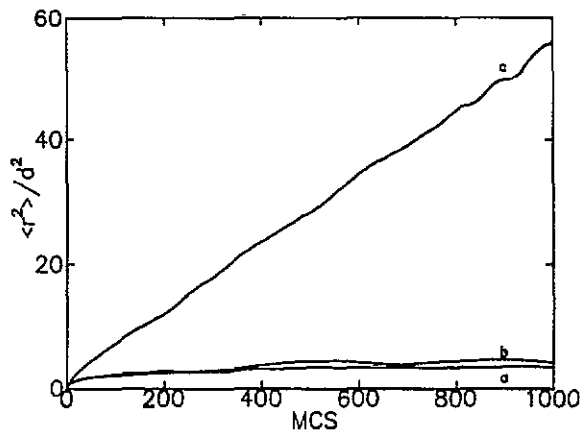


Figure 4. Mean square displacement ($\langle r^2 \rangle$) as a function of MCSs for monodisperse suspension. Curves labelled *a*, *b* and *c* correspond to the same parameters as those of figure 3.

pseudobinary. This pseudobinary distribution gives an equimolar AB alloy ($A_{0.5}B_{0.5}$). It is probably more meaningful to consider other kinds of charge ordering (such as AB_n type) in a strict binary system with δ function distributions. Further, if one has to examine the AB_n type of ordering in an equimolar alloy, this will necessarily make the system multiphase. Such problems of multiphase coexistence cannot be handled with a system size of 432 and hence were not attempted.

3. Results on monodisperse and charge polydisperse colloids

Dilute aqueous suspensions of monodisperse (CPD = 0) polystyrene colloidal particles are known to crystallize into BCC order [8, 9, 18, 19] upon deionization. MC simulations of Tata and Arora [9] have shown that for impurity ion concentration $n_i = 0$, the suspension with $n_p = 1.33 \times 10^{12} \text{ cm}^{-3}$ exhibits a BCC crystalline order and melts at $n_i \geq 1.4n_p Z_0$. A charge polydisperse system with 24% CPD also exhibits a marginally disordered crystalline solid at $n_i = 0$ which melts at $n_i > 0.85n_p Z_0$. These MC simulations are based on the Metropolis algorithm and guarantee reaching a stable equilibrium state. However, it is also likely that the system may get trapped in a metastable state for a long time especially when one is close to a phase transition as mentioned earlier. In certain cases one may not be able to evolve to the final stable equilibrium state due to insufficient computer run-time. In such cases by choosing widely different initial states and evolving for long enough time one can judge whether the final state reached in a MC simulation is a stable equilibrium state (this is also referred to as the ground state or low-temperature state) or not.

MC simulations have been carried out for monodisperse (CPD = 0) and charge polydisperse (CPD = 24%) colloids at $n_i = 0$ by choosing the initial configurations as (1) a BCC lattice and (2) a liquid-like ordered configuration. From these initial configurations both systems have been evolved and the results are as follows.

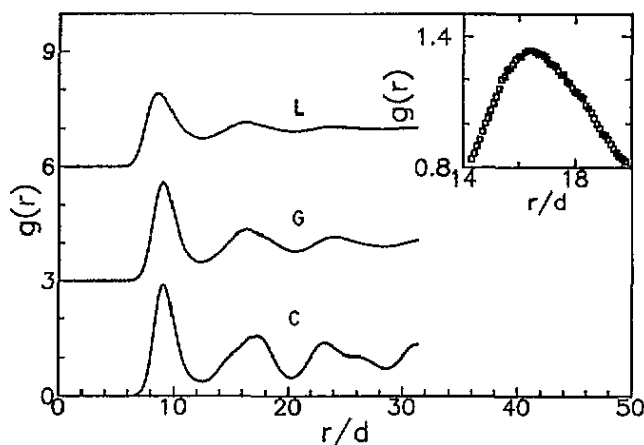


Figure 5. $g(r)$ versus r for 24% charge polydisperse system. Curve *C* is for a system evolved from initial BCC configuration at $n_i = 0$. Curve *G* corresponds to the system evolved from a liquid-like ordered initial configuration after quenching to $n_i = 0$. $g(r)$ corresponding to the initial state for curve *C* (liquid-like ordered suspension at $n_i = 2.6n_p Z_0$) is also shown as curve *L* for the sake of comparison. For clarity the distortion in the second peak of curve *G* is shown as the inset.

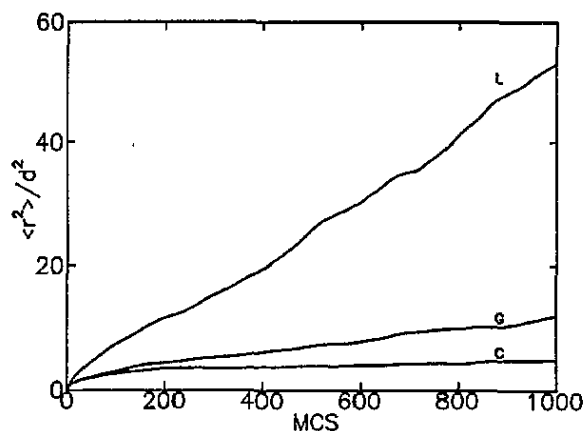


Figure 6. Mean square displacement as a function of MCSs for 24% CPD system. The parameters of curves *C*, *G* and *L* are the same as those in figure 5.

3.1. Monodisperse suspensions

Figure 3 shows the pair correlation functions for a monodisperse suspension with $n_i = 0$, calculated after reaching equilibrium from the respective initial configurations. The initial liquid-like ordered configuration is prepared by performing simulations at $n_i = 2.6n_p Z_0$. The inset in figure 3 shows the coordinate-averaged pair correlation function $G(r)$ obtained by averaging the coordinates over a sufficiently large number of configurations (i.e., time averaged) [9, 20]. The $G(r)$ thus obtained is free from thermal broadening and helps in identifying the crystal structure unambiguously. It is clear from figure 3 (curves *a*, *a'*, *b* and

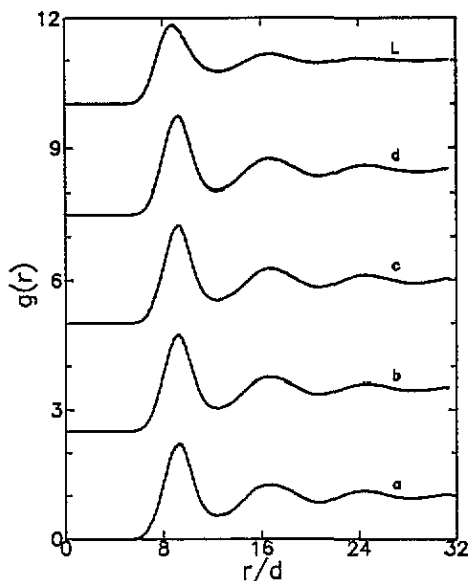


Figure 7. $g(r)$ versus r for 34% randomly distributed charge polydisperse system obtained from different initial configurations and also by simulated annealing. Curves a , b and c are obtained by evolving from BCC and FCC at $n_i = 0$ and from liquid-like ordered initial configurations after quenching to $n_i = 0$, respectively. Curve d is obtained from simulated annealing until $n_i = 0$ (for details, see text (section 5)). The $g(r)$ corresponding to the initial state for curve c (liquid-like ordered suspension at $n_i = 2.6n_p Z_0$) is also shown as curve L for the sake of comparison. Curves b , c , d and L are shifted vertically by amounts 2.5, 5, 7.5 and 10 respectively for the sake of clarity. It may be mentioned that curves a , b , c and d are indistinguishable within the statistical accuracy, when superimposed.

b') that the equilibrium state for a monodisperse suspension with n_i obtained from the two initial configurations is BCC crystalline. Another parameter that is used in simulations to characterize the solid is the behaviour of the mean square displacement, $\langle r^2 \rangle$, as a function of MCSS. Figure 4 shows the saturation behaviour of the mean square displacement (curves a and b) as a function of MCSS, as expected for a crystalline solid. For the sake of comparison the $g(r)$ and mean square displacement as function of MCSS of the liquid-like ordered suspension at $n_i = 2.6n_p Z_0$ (i.e., the initial state for curve b) are also shown in Figs. 3 and 4 (curve c) respectively. It is worth pointing out the important difference between the two crystalline states obtained by evolving from two widely different initial configurations. The BCC crystalline state obtained by evolving from the initial BCC lattice is expected to be a single crystal, whereas that obtained by evolving from the liquid-like ordered initial configuration is expected to be either polycrystalline or glassy. This is because evolving from such an initial configuration corresponds to quenching. If the amount of quenching is sufficient to avoid nucleation, the system freezes into a glass; otherwise, it crystallizes with defects such as grain boundaries. In charge-stabilized colloids, decreasing impurity ion concentration is analogous to reducing the effective temperature T^* (defined as $k_B T/U_a$, where U_a is the interaction energy at average interparticle separation a_s) [8, 9]. The rate at which n_i is lowered determines the rate of cooling in these systems. Although the MC technique lacks a strict or rigorous sense of time scale, still it is meaningful to consider a MC step as one arbitrary time unit. Then the lowering of impurity from $2.6n_p Z_0$ to zero in

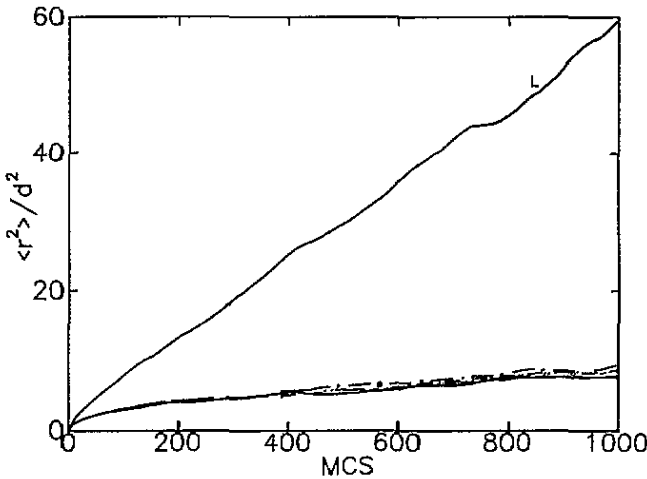


Figure 8. Mean square displacement as a function of MCSs for 34% CPD system. The parameters of curves drawn as solid, dashed, dash-dot-dot-dash and dot-dash correspond to those of curves *a*, *b*, *c* and *d* of figure 7 respectively. The parameters of the curve *L* are the same as those of curve *L* in figure 7.

one step corresponds to a cooling rate (Q_r) of 0.32/MCS. Thus evolving from a liquid-like ordered initial configuration corresponds to a Q_r of 0.32/MCS and equilibrating the system at an effective temperature of 0.04 corresponding to $n_1 = 0$. Since the first peak height S_{\max} of the structure factor is expected to be different for a single crystal and polycrystalline systems, S_{\max} has been calculated at scattering vector $Q = (2\pi/l)(1, 1, 0)$, where l is lattice constant. The structure factor is given by

$$S(Q) = 1 + \frac{1}{N} \sum_{i \neq j}^N \exp[-iQ \cdot (r_i - r_j)]. \quad (8)$$

The value of S_{\max} is obtained by averaging $S(Q)$ calculated for all possible vectors Q whose magnitude is the same (i.e., it amounts to taking all possible orientations). The S_{\max} thus obtained for the system evolved from BCC is found to be ~ 310 and that evolved from the other initial configuration is approximately three. These values clearly indicate that the crystalline state which yielded a high value of S_{\max} is a single crystal and the other is polycrystalline. The asymptotic value of the mean square displacement being more in the case of polycrystalline sample (curve *b*) as seen in figure 4 as compared to the single crystal (curve *a*) is due to the diffusion of the particles at the grain boundaries.

3.2. Suspensions with polydispersity less than critical CPD

Similar to the simulations on monodisperse systems, simulations have also been carried out at 24% CPD by taking the initial configurations as BCC and liquid-like order. The latter configuration is prepared by performing simulations at $n_1 = 2.6n_p Z_0$. The pair correlation functions are shown in figure 5 and the behaviours of the mean square displacement in figure 6. From the characteristic crystalline peaks in $g(r)$ (curve *C*) shown in figure 5 and the saturation behaviour of the mean square displacement (curve *C*) seen in figure 6 one can conclude that this system when evolved from the BCC initial lattice is a marginally ordered

crystalline solid. On the other hand, the one evolved from the liquid shows distortion in the second peak (split second peak) in the $g(r)$ (curve G ; see also the inset in figure 5) characteristic of glassy order obtained by quenching. The tendency towards saturation of the mean square displacement (curve G) as seen in figure 6 also indicates that it is a solid. Thus for 24% CPD the system evolves from a liquid state to glass but not to a polycrystalline state. It may be mentioned that Brownian dynamic simulations of Löwen *et al* [5] for a charge polydisperse system also yielded a split second peak for the glassy state obtained by quenching from a liquid. The split second peak in the present case is not as sharp as that seen in some of the atomic glasses. This is because of the presence of static disorder induced by CPD. If the static disorder is too large (for values beyond critical CPD), the splitting gets smeared out resulting in an amorphous state with a smooth second peak [9]. Thus for 24% CPD and $n_i = 0$, evolving from two different initial configurations leads to two different equilibrium structures: one is stable (crystalline) while the other is metastable (glass). Notice that the same cooling rate of 0.32/MCS is sufficient to produce a glassy state for 24% CPD suspension indicating that the glass transition temperature of a charge polydisperse system is higher than that corresponding to a monodisperse system. This is understandable from the fact that, in atomic systems, the larger the number of components, the easier it to form a glass.

3.3. Suspensions with polydispersity greater than critical CPD

Simulations [8, 9] have also revealed that the suspension with 34% CPD and $n_i = 0$, when evolved from a BCC initial configuration, becomes disordered. This disordered structure is found to be amorphous [9]. In order to find out whether this amorphous state is thermodynamically stable or metastable, simulations are carried out by evolving from a liquid-like ordered initial configuration as well as another initial configuration where particles ($N = 500$) have been arranged on a face-centred cubic (FCC) lattice with charges being randomly distributed. Figure 7 shows the pair correlation functions and figure 8 the behaviour of the mean square displacement. Note that (figure 7) $g(r)$ functions obtained from three different initial configurations are identical (BCC: curve a , FCC: curve b and quenched: curve c) and do not exhibit characteristic crystalline peaks. Further, the mean square displacement of these systems also exhibits a tendency towards saturation (solid, dashed and dash-dot-dot-dash curves) as seen in figure 8, and also the amount of the mean square displacement at the end of 1000 MCS is much less than the average interparticle separation a_s ($n_p^{-1/3} = 8.3d$). These results unambiguously suggest that the disordered state is amorphous. As mentioned earlier in the MC simulation based on the Metropolis algorithm, if the final state is the same irrespective of the initial state, it is possible to conclude that this final state is a thermodynamically stable state, hence the amorphous state obtained might be a stable equilibrium state. Note from figure 7 that, in contrast to the 24% CPD system, $g(r)$ of a system at 34% CPD obtained by quenching from a liquid-like state (curve c) does not show a split second peak. Another important difference worth pointing out is that the 24% CPD glass has a corresponding BCC crystalline state which is stable as seen in section 3.2. On the other hand we have seen that for 34% CPD evolving even from a BCC initial configuration results in an amorphous structure. Since evolving from BCC is not a quenching, it can be concluded that suspension with 34% CPD does not require any quenching to form an amorphous structure. The rapid cooling from a liquid-like state has also resulted in a disordered structure identical to those evolved from BCC or FCC. We now present further results and arguments to emphasize that the amorphous state obtained for 34% CPD is different from conventional glasses and is a stable state.

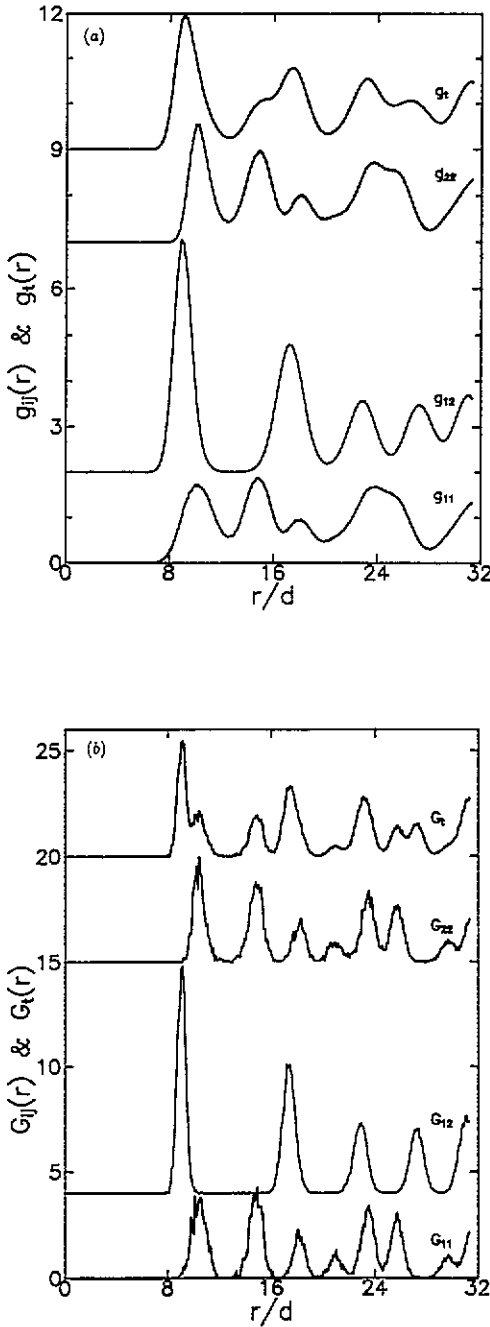


Figure 9. (a) Partial correlation functions $g_{ij}(r)$ and total correlation function $g_t(r)$ for a charge-ordered system with 34% CPD at $n_1 = 0$. (b) Coordinate-averaged partial correlation functions $G_{ij}(r)$ and total correlation function $G_t(r)$ for the charge polydisperse suspension whose parameters are same as those in (a). Coordinate averaging is done over 2000 MCSS.

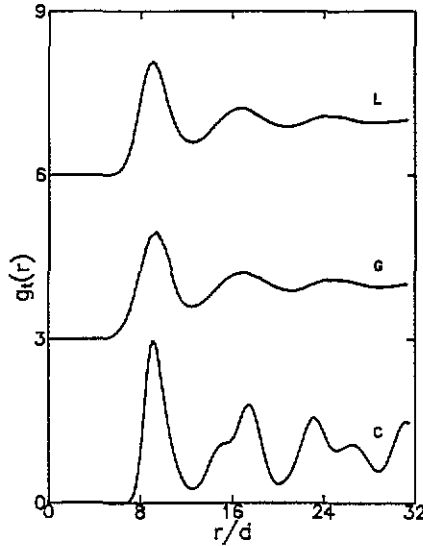


Figure 10. The total pair correlation function $g_l(r)$ as a function of r for equilibrium states obtained from a charge-ordered initial configuration. Curve C is for $n_1 = 0$ and CPD = 34%, curve G is for $n_1 = 0$ and CPD = 43% and curve L is for $n_1 = 0.8n_p Z_0$ and 34% CPD.

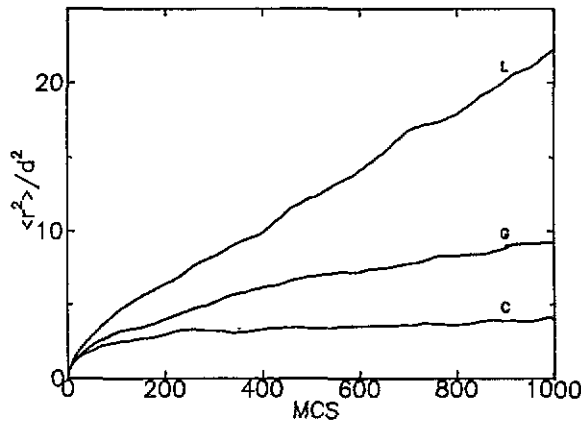


Figure 11. The mean square displacement as a function of MCS for the suspensions with charge-ordered initial configuration. The parameters of the curves C, G and L are the same as those in figure 10.

4. Results for the charge-ordered state

Löwen *et al* [6] have conjectured that the suspensions with large charge polydispersity prefer charge ordering (small charges as first neighbours around a large charge and vice versa) to lower the free energy. In order to investigate whether such an equilibrium state exists for 34% CPD, and also to know the stability of such a charge-ordered state, MC simulations have been carried out for different n_1 values by preparing a CsCl-type charge-ordered initial

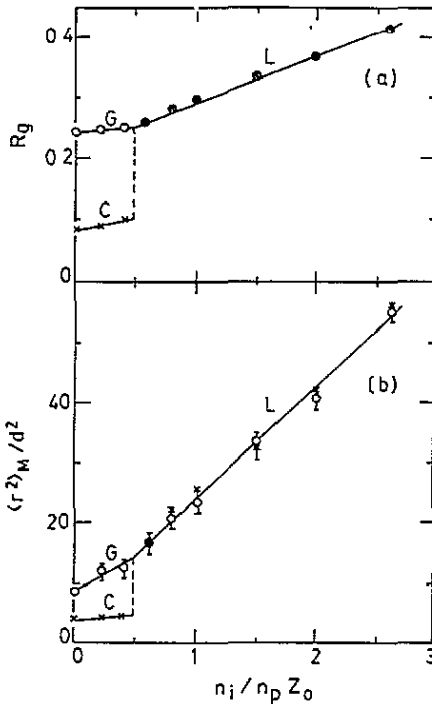


Figure 12. (a) Structural parameter R_g and (b) the extent of mean square displacement after 1000 MCSS as a function of n_i . (x) charge-ordered state, (o) simulated annealing (for details, see text (section 5)). The regions labelled as C, G and L represent crystalline, amorphous (glassy) and liquid-like states respectively.

state. The extent of charge ordering is characterized by calculating partial pair correlation functions and the Warren–Cowley short-range order parameter as described in section 2.

Figure 9 shows the pair correlation functions for the charge ordered state. It is obvious from the partial correlation functions $g_{ij}(r)$ and the sharp peaks in coordinate-averaged partial correlation functions $G_{ij}(r)$ that for 34% CPD, when evolved from a charge-ordered initial state, the system reaches a crystalline equilibrium state. The value of α is also found to be -1 , indicating that the system remains charge ordered. In order to find out the stability of this charge-ordered crystalline state against melting, simulations have been carried out for different n_i and the results are shown in figures 10 and 11. One can identify the structure at $n_i = 0.8n_p Z_0$ to be liquid-like ordered from the absence of sharp peaks in $g_t(r)$ as seen in figure 10 (curve L) and from the linear behaviour of the mean square displacement shown in figure 11 (curve L). For comparison $g_t(r)$ and $\langle r^2 \rangle$ for the charge-ordered crystal are also shown in figures 10 and 11. Note the sharp peaks in $g_t(r)$ and the saturation behaviour of the mean square displacement (curves labelled as C). Thus the charge-ordered state has melted at $n_i = 0.8n_p Z_0$. Since the colloidal system simulated is polydisperse only in charge and not in size, it is sufficient to calculate a structural parameter, R_g (defined as the ratio of the height of the first minimum to that of the first maximum of $g_t(r)$) and a dynamical parameter $\langle r^2 \rangle_M$ (i.e., the extent of the mean square displacement at the end of $M = 1000$ MCS) to identify the melting. These are shown in figure 12. It may be

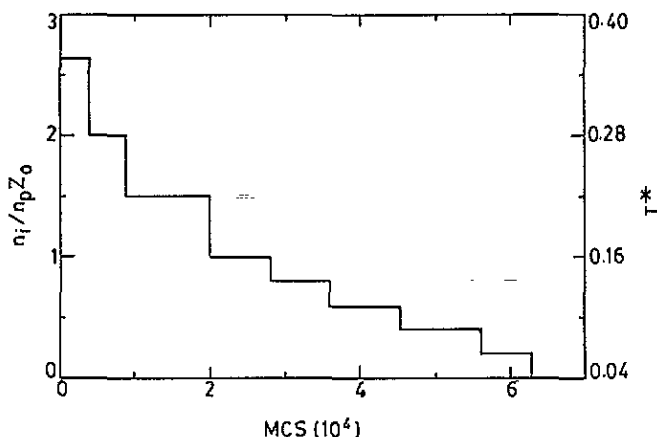


Figure 13. The simulated annealing schedule for randomly distributed 34% charge polydisperse system. The effective temperature T^* corresponding to each impurity ion concentration (n_i) is also shown on the right-hand side of the y axis.

mentioned that these parameters have been extensively used for identifying the melting of both crystalline and amorphous colloidal [8, 9, 15] and atomic systems [21, 22]. Notice from figure 12 that both R_g and $\langle r^2 \rangle_M$ show a jump at around $0.45n_p Z_0$ indicating the melting of charge ordered crystal. We have earlier studied the melting of monodisperse and randomly distributed charge polydisperse colloidal crystals [8, 9, 15]. For the same values of n_p , d and Z_0 the monodisperse colloidal crystal is found to melt at $1.45n_p Z_0$ and the 24% CPD charge polydisperse crystal at $0.75n_p Z_0$. The randomly distributed charge polydisperse (34% CPD) amorphous solid is found to melt at around $1.5n_p Z_0$. From these results it can be concluded that the 34% charge-ordered colloidal crystal is relatively unstable as compared to the amorphous state as one requires rather a small amount of impurity ion concentration to disrupt the crystalline order. One can also notice from figures 10 and 11 that the crystalline state gets disordered by increasing CPD to 43% at $n_i = 0$ (curves G). This disordered state is a solid because (a) the strength of interaction is not changed (the inverse Debye screening length is the same), (b) the mean square displacement exhibits a tendency towards saturation and (c) the extent of the mean square displacement (at 1000 MCSs) is much smaller than a_s . Thus the MC simulations on the charge-ordered state corresponding to 34% CPD reveal that the charge-ordered state is unstable against disordering. Apart from CPD the stability of charge ordering may strongly depend on the screening length (K^{-1}) used in (1). It may be mentioned that the pair correlation function, mean square displacement and R_g calculated for n_i values greater than $0.8n_p Z_0$ (i.e., for liquid-like ordered suspensions) are found to be same for equilibrium states evolved for both random and charge-ordered initial configurations. Since the liquid-like ordered states are identical, it is worth asking a question: when such a state is slowly cooled (i.e., by lowering the impurity ion concentration) and annealed to an effective temperature $T^* = 0.04$ corresponding to $n_i = 0$, will it evolve to a charge ordered state or a disordered state? In order to answer this question, simulated annealing studies are carried out and the results are discussed in the next section.

5. Simulated annealing and results

We have seen in the earlier sections that for 34% CPD and $n_i = 0$, the equilibrium state of the colloidal system depends on the manner in which the charges are arranged on the lattice in the initial configuration. If the charges are randomly distributed, the simulations resulted in a disordered state and when charges are arranged in a CsCl-type structure a charge-ordered crystalline state is obtained. The only way to find out the low-temperature state (ground state) for a random charge distribution is by performing simulated annealing studies [23]. The simulated annealing process [23] consists of first 'melting' the system at high effective temperature (this is achieved in charge-stabilized colloids by increasing the impurity ion concentration n_i) and then lowering the temperature (n_i) in gradual stages until the system 'freezes' and no further changes occur. At each temperature (n_i), the evolution is carried out for long enough time for the system to reach steady state. The sequence of temperatures and the number of MCSS evolved to reach equilibrium at each temperature (in other words at each n_i) form the annealing schedule. Forming an annealing schedule is specific to the system and is usually done empirically. Since we have some knowledge about the melting of monodisperse as well as polydisperse colloids from our earlier simulation work [8, 9, 15] we have chosen the annealing schedule shown in figure 13. Notice that the simulated annealing is started from a liquid-like ordered suspension having $n_i = 2.6n_p Z_0$ and CPD = 34% and charges assigned randomly. The simulations have been carried out for sufficiently long times at each impurity ion concentration, keeping in view the slowing down of the MC evolution process across freezing/melting [15]. At every stage after equilibration pair correlation functions, structural parameter R_g , $\langle r^2 \rangle_M$ and the short-range order parameter α are calculated to identify the freezing, the structure and the extent of charge ordering. The partial pair correlation functions and value of α indicated no signature of charge ordering. The behaviour of R_g and $\langle r^2 \rangle_M$ obtained from simulated annealing are also shown in figure 12 (circles) and compared with those for the charge-ordered state. The change in the slope at around $0.45n_p Z_0$ suggests the freezing of the charge polydisperse liquid into a solid. The shape of $g(r)$ of the state obtained from simulated annealing to $n_i = 0$ (curve *d*) seen in figure 7 and its mean square displacement behaviour shown in figure 8 (dot-dash curve) suggest that it is an amorphous solid and also the same as those obtained by evolving from other initial configurations discussed earlier. Thus simulated annealing studies also result in only a disordered state and not a charge-ordered crystalline state. It can be seen from figure 12(b) that the value of $\langle r^2 \rangle_M$ is higher in the disordered state as compared to the charge-ordered crystalline state. It is well known in atomic glasses that the diffusion constant in amorphous systems is large as compared to the crystalline states [24]. This is because a glassy structure has more free volume as compared to the crystalline counterpart. Further the mechanisms of diffusion are also different. Another important point to be noted is that the crystalline structure simulated here is also free from defects (e.g. vacancies). Hence the vacancy-assisted diffusion is also prevented. Thus the behaviour of the mean square displacement seen in figure 12 is understandable. We have also carried out simulations by taking the $0.8n_p Z_0$ charge-ordered liquid as the initial configuration and slowly cooling to $n_i = 0$ (by reducing n_i in steps of $0.2n_p Z_0$ and evolving for long times). This did not freeze into the charge-ordered crystalline state either and $g(r)$ and the mean square displacement as a function of MCS are found to be the same as those of the random disordered state. Also α is found to be close to zero suggesting no charge ordering. As mentioned earlier if AB_n -type ordering existed in the equilibrated cell, partial correlation functions would have shown the signatures of this ordering. However, except for a smooth behaviour no other feature is found in the

calculated partial correlation functions from simulated annealing data.

6. Discussion and conclusions

Present simulations on the charge polydisperse system having 34% CPD and $n_i = 0$ reveal that, when charges are randomly distributed, the lowest-temperature state (ground state) is always a disordered state (amorphous-like) and is different from the glassy state obtained by quenching. In order to understand why the simulated annealing results have not yielded a charge-ordered state, we have also calculated the free energy F by computing the total interaction energy U_T and the entropy S (details of the entropy calculation are given in [11]). The free energy obtained as $F = U_T - TS$ for a charge-ordered crystalline state is found to be $131.5Nk_B T$ and for the random disordered state it is $126.3Nk_B T$. Since the free energy of the charge-ordered state is greater than that of the random disordered state the end result of simulated annealing is understandable. In order to see whether the 34% CPD system favours phase separation into regions of large and small charges, we have carried out simulations with half the cell occupied with low charges and the other half filled with large charges [25]. Use of periodic boundary condition transforms the system into a layered structure. The free energy estimated is found to be much higher than that of the charge-ordered state as well as that of the randomly distributed charge state. Hence, this being the ground state is also ruled out. In addition to this, our simulated annealing studies do not show either any signature of phase separation. Apart from simulated annealing, since other simulations from different initial configurations (i.e., BCC, FCC and from a liquid-like ordered initial state) also yield only a disordered solid for 34% CPD and $n_i = 0$, it may be concluded that the disordered state for randomly distributed charge is the ground state and hence the *stable* state of the system.

The only glassy system among atomic systems that is known to be stable is a 'spin glass' [26]. This system has 'quenched-in randomness' and 'frustration' arising due to interactions favouring different and incompatible kinds of spin ordering simultaneously [23, 26]. A glassy state of this type does not need any quenching, hence one can discuss the possibilities of an equilibrium phase transition [26] unlike the conventional glass transition. In analogy, the charge polydisperse amorphous state for 34% CPD also has static disorder (quenched-in disorder) arising from the randomness in the interactions. The interactions are random because every pair interaction U_{ij} is different due to the charges being different. Arora and Tata [11] have considered a nearest-neighbour model and calculated the lattice relaxations occurring due to randomness in nearest-neighbour interaction. It is shown that the critical CPD of 26% corresponds to a polydispersity of 37% in interactions and 17% in polydispersity of effective hard-sphere diameters associated with various charges [9]. In the effective hard-sphere model it is argued that frustration in packing of these effective hard spheres causes the disruption of crystalline order resulting in an amorphous state. Thus this frustration in packing is analogous to frustration in alignment of spins in the spin glass. It is clear from present simulations as well as earlier-reported results [8, 9] that one does not need quenching to obtain the amorphous state at large values of CPD ($> 24\%$). Quenching is not required because there are not many particles of the same charge and also the magnitude of the difference in charges is large for large values of CPD, causing the suppression of nucleation to form crystallites. It may be mentioned that in the case of CPD less than critical CPD one obtains a crystalline state. This is because the magnitude of the difference in neighbouring charges is not large enough to disrupt the long-range order. It is shown [11] that the root mean square displacement of equilibrium positions is only 0.23 of the nearest-neighbour distance for CPD less than 26%. Thus the present results and the

above analogy with a spin glass suggest that the amorphous state obtained for 34% CPD is a stable state and not a metastable state.

To conclude, we have shown that irrespective of the initial configuration a monodisperse colloidal suspension freezes into a BCC crystalline order for low volume fractions. If the starting configuration is liquid-like one obtains a polycrystalline state. Although evolving from a liquid-like state is equivalent to quenching, the cooling rate is not sufficient to suppress the nucleation. In the case of a charge polydisperse system, if the CPD is less than critical CPD the final equilibrium state depends on the initial state configuration. It is shown that for 24% CPD evolving from BCC results in a marginally disordered crystalline state and evolving from a liquid-like initial configuration results in a glassy state with a split second peak. This is analogous to the conventional glass obtained by quenching. On the other hand, for large values of CPD (greater than critical CPD) irrespective of the initial configuration it always evolves to a *stable* amorphous state. It is argued that this amorphous state is analogous to a spin glass in terms of frustration, frozen (static) disorder and also does not require quenching.

The behaviour of magnetic susceptibility with temperature has been used to characterize the spin glass state. It is worth exploring the analogous quantity in the case of charge polydisperse glass, although when charges are arranged in a charge-ordered initial state and the system is evolved, it results in a charge-ordered state which is found to have free energy higher than that of a disordered state with random charge distribution. It is also relatively unstable with respect to n_i and CPD.

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