Crystalline-to-glass transition in charge polydisperse colloids

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Abstract. The crystalline-to-glass transition in dilute charge polydisperse colloidal suspensions is investigated using Monte Carlo simulations assuming pairwise additivity of the interaction. The time averaging of coordinates is used to reduce the broadening of the pair correlation function due to random thermal motion. The suspension is found to remain crystalline at low polydispersities and becomes disordered at large charge polydispersities (CPDs). The behaviour of particle diffusion in the suspension is used to characterize the disordered state as glass. The dependence of structural parameters such as S_{max}, g_{min}/g_{max} and particle diffusion suggests that the transition occurs at 26% CPD. The polydispersity of effective hard-sphere diameters is obtained and compared with that of a size polydisperse system.

1. Introduction

A glassy state can be produced in a number of ways, e.g. by quenching of liquids, by vapour deposition on a cold substrate, by pressure-induced amorphization of crystalline solids and by ion implantation [1–4]. In the case of glasses obtained by quenching of a liquid, it is well known that, the larger the number of components, the easier is the formation of glass. Apart from the different atomic sizes (polydispersity) arising owing to different components, the nature of bonding (interaction) also plays an important role in determining the glass-forming tendencies [5]. Colloidal suspensions, which are known to exhibit structural ordering similar to those in atomic systems [6], are ideal systems for investigating the effect of polydispersity on the stability of crystalline order for the following reasons: polydispersity is inherent in colloidal systems, i.e. even the so-called monodisperse colloids have a certain degree of size polydispersity (SPD) and charge polydispersity (CPD); it is possible to control the size of the particles and the charge on them rather independently and consequently their polydispersities. Separate investigations of the effect of SPD (which determines the randomness in size) and the effect of CPD (which determines the randomness in interaction) on the stability of the crystalline order would yield valuable information on the relative importance of these towards the formation of glassy order. Recent investigations show that SPD beyond 11% disrupts the crystalline order [7–9], whereas the role of CPD has not been investigated yet.

Glass-like ordering has been reported in a number of monodisperse [10–12] and binary colloids [13–16]. In concentrated suspensions, SPD is believed to be the dominating factor in disrupting the crystalline order [7, 8]. However, it has been recognized that SPD has little effect in determining the structural ordering in dilute charged colloids [7]. This is because, in a strongly interacting dispersion, particles cannot come

close to each other because of strong Coulomb repulsion. The effective hard-sphere diameter h of a particle could be several times the actual diameter. As the charge on the particle determines h, CPD is expected to be the deciding factor in disrupting the crystalline order in charge polydisperse systems. The effect of CPD is even more important in binary colloids which have both SPD and CPD. Recently Löwen *et al* [17] have investigated the dynamical aspects of the liquid-to-glass (L→G) transition in a charge polydisperse colloidal suspension; however, the critical polydispersity which inhibits nucleation (crystallization) has not been obtained. In this paper we report a detailed investigation of the CPD-driven crystalline-to-glass (C→G) transition using Monte Carlo (MC) simulation. The study of such systems would provide a better understanding of the glassy phase in general.

In the present work, MC simulations are carried out on dilute aqueous colloidal suspensions with varying degrees of CPD while keeping the average strength of interaction constant. The pair correlation function $g(r)$, mean square displacement (MSD) $\langle r^2 \rangle$, height S_{max} of the first peak of the structure factor, osmotic pressure P and total interaction energy U_T per particle are obtained. As the CPD is increased, the resulting equilibrium structures are characterized and the states of the suspension are identified on the basis of the behaviour of $g(r)$, MSD and S_{max}. The effective hard-sphere diameter and its polydispersity (the effective size polydispersity (ESPD)) are obtained.

2. Simulation details

MC simulations based on the Metropolis algorithm for a canonical ensemble [18] (constant NVT) are done to simulate an aqueous colloidal suspension of particles of diameter d (= 109 nm) interacting via a hard-sphere repulsion plus a size-corrected Yukawa pair potential $U(r_{ij})$ given as

$$U(r_{ij}) = \begin{cases} \infty & r_{ij} \leqslant d \\ Z_i Z_j e^2 [4 \exp(Kd)/(2 + Kd)^2] \exp(-Kr_{ij})/\epsilon r_{ij} & r_{ij} > d \end{cases}$$

where Z_i and Z_j are the charges (expressed in units of electronic charge e) on particles i and j, respectively, with a centre-to-centre distance r_{ij}. K, the inverse Debye screening length, arising owing to the counter-ion concentration $n_p Z_0$ and impurity ion concentration n_i, is given as $K^2 = 4\pi e^2 (n_p Z_0 + n_i)/\epsilon k_B T$ where n_p is the particle concentration, Z_0 the average charge, k_B the Boltzmann constant, ϵ the dielectric constant of water and T the temperature (298 K). Z_0 is taken to be 600 [14] and $n_i = 0$. In order to simulate a charge polydisperse system, charges on the particles are assigned randomly from a symmetric rectangular distribution with mean Z_0 and width 2Δ. CPD is defined as the standard deviation relative to the mean, i.e. σ_Z/Z_0, which is $\Delta/3^{1/2} Z_0$ in this case. As the average charge Z_0 is kept fixed throughout the simulation, the average strength and the range of the interaction remain constant and hence only the effect of polydispersity is manifested. The temperature is also kept fixed throughout the simulations. Simulations are done on a cubic cell containing N particles ($N = 250$ and 432) using periodic boundary conditions. The size L of the cell is chosen to correspond to $n_p = 1.33 \times 10^{12}$ cm^{-3} (volume fraction $\varphi \simeq 10^{-3}$). Starting configurations are always chosen as body-centred cubic (BCC) because, at low volume fractions, only the BCC structure has

been found to be stable [19]. The total interaction energy $U_T(r_1 \ldots r_N)$ is obtained by assuming pairwise additivity of interaction. When the range K^{-1} of the interaction is large compared with the average interparticle separation $a_s = n_p^{-1/3}$, i.e. $Ka_s < 1$, many-body interactions also become important. However, in the present case, $Ka_s = 2.44$ makes the pairwise additivity a reasonable assumption. The step size is $0.5d$. Most of the suspensions away from the transition took approximately 9×10^5 configurations to reach equilibrium while those close to the transition took 6×10^6. The trial rejection ratio after reaching equilibrium is around 50%. An MC step (MCS) is defined as a set of N configurations during which, on an average, each particle gets a chance to move. After reaching equilibrium, $g(r)$ is calculated with an interval $\Delta r = 0.1d$ using the standard method [20] and averaged over 1.5×10^5 configurations. The virial equation is used to obtain P [18]. The MSD is obtained using $\langle r^2(m) \rangle = (1/N) \sum_{j=1}^{N} [r_j(m+n) - r_j(n)]^2$ after reaching equilibrium. In order to reduce statistical fluctuations, the MSD is averaged over 50 different choices of initial frame n. The colloidal system simulated here is polydisperse in charge but not in size. Hence it is sufficient to describe the system in terms of the number–number structure factor $S(Q)$ and $g(r)$ [21]. $S(Q)$ is calculated at a few selected wavevectors using the expression $S(Q) = \langle \rho_Q \rho_{-Q} \rangle / N$, where $\rho_Q = \sum_{j=1}^{N} \exp(-iQ \cdot r_j)$ and $\langle \ldots \rangle$ represents the ensemble average. The results, i.e. $g(r)$, MSD, etc, obtained with 432 particles are the same as those obtained for 250 particles within statistical error. For example, the heights of the first peak of $g(r)$ are 3.50(7) and 3.55(7) for $N = 432$ and 250, respectively. In fact the $g(r)$-values obtained in the two cases are essentially indistinguishable. Similarly the MSDs after 1000 MCSs are $3.3(3)d^2$ and $2.8(3)d^2$ for the two system sizes. This suggests that even 250 particles are adequate. However, the results reported here correspond to 432 particles.

3. Results and discussion

A disordered (non-crystalline) material is called a glass if it exhibits rigidity [14] or if the MSD of the atoms exhibits a saturation-like behaviour in time and the root MSD (RMSD) is much smaller than the nearest-neighbour distance d_{nn} [11, 16]. On the other hand a liquid is expected to show fluidity or a non-saturating linear dependence of MSD in time (diffusive behaviour). The disappearance of characteristic peaks in $g(r)$ or in $S(Q)$ of a solid is often taken as the onset of glassy order [3]. Figure 1 shows $g(r)$ for systems with different CPDs. Note that the monodisperse suspension (0% CPD) and that at 24% CPD exhibit peaks characteristic of the crystalline order whereas these are not present in the $g(r)$ for the system with 28% CPD, suggesting that this system is probably disordered. Note from figure 1 that, as expected, the peaks in $g(r)$ are broader for suspensions with a finite CPD. Apart from the CPD, as the simulations are carried out at 298 K, the thermal vibrations of particles also contribute to the broadening of the peaks in $g(r)$. The effect of the CPD on $g(r)$ can be seen more clearly if thermal broadening can be minimized. In computer experiments the effect of temperature on the $g(r)$ of solids (thermal broadening) can be easily minimized if the particle coordinates are time averaged over a sufficiently large number of configurations [22]. The pair correlation function $g_c(r)$ obtained from such an averaged frame is expected to show sharp peaks for a monodisperse suspension. In order to characterize the state of the suspension with CPD unambiguously, the $g_c(r)$-values for different CPDs are obtained and are shown in figure 2.

Approximately 5×10^5 configurations are found to be adequate for averaging. Sharp peaks corresponding to 12 neighbour shells of BCC structure are seen for zero CPD. For suspensions with CPD the peaks corresponding to different neighbour shells slowly broaden with increasing CPD and merge with other prominent peaks. In the case of systems up to 24% CPD the broadened peaks still correspond to the underlying BCC lattice, suggesting that, although the system is marginally disordered, one can still describe the structure in terms of an overall crystalline lattice. However, at 28% CPD, $g_c(r)$ exhibits smooth second and third peaks whose positions do not correspond to the crystalline structure. This confirms the conjecture that the structure obtained at 28% CPD is non-crystalline, i.e. disordered.
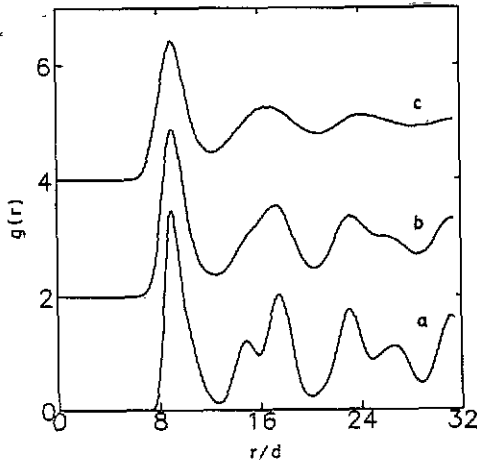

Figure 1. Pair correlation functions for suspensions with different CPDs: curve (a), 0% CPD; curve (b), 24% CPD; curve (c), 28% CPD. The $g(r)$-values corresponding to 0% and 24% CPD exhibit features characteristic of crystalline order (distortions around second and third peaks) whereas that for 28% CPD appears disordered (smooth peaks).
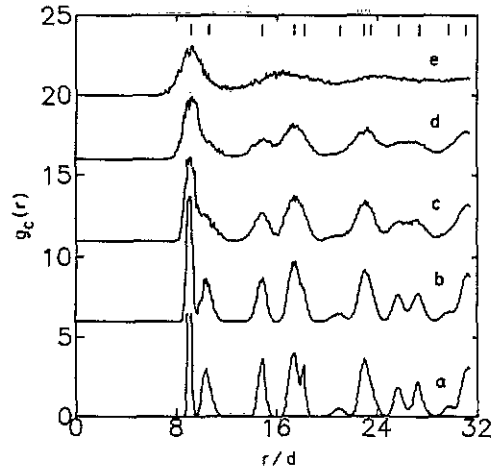
Figure 2. Pair correlation functions $g_c(r)$ obtained from time-averaged particle coordinates (averaged over 0.5 million configurations) for various CPDs: curve (a), 0% CPD (the height of the first peak is 13.8); curve (b), 9.4% CPD; curve (c), 17% CPD; curve (d) 24% CPD; and curve (e), 28% CPD. The vertical bars correspond to the positions of different neighbour shells for the ideal BCC structure.

The disordered state found at 28% CPD could be either a solid (glass) or a liquid. As the average charge Z_0 and hence the range K^{-1} and the average strength of interaction are kept constant all through the simulations, the system is expected to remain a solid even when the CPD is varied. For the zero-CPD suspension, $U_T \simeq 138 k_B T$ and $P \simeq 197 n_p k_B T$, and these quantities do not show significant variation when the CPD is increased, whereas monodisperse colloidal crystals have been found to melt only when n_i is increased and, at melting, $U_T \simeq 25 k_B T$ [21]. Such high values of U_T and P in a CPD colloid suggest that the system, although disordered, must be solid-like. Alternatively, it is often convenient to define a reduced temperature $T^* = k_B T / U(a_s)$ where $a_s = n_p^{-1/3}$ is the natural length scale in the suspension. For the systems considered here, $T^* \simeq 0.04$ [21]. It has recently been shown that a suspension with a sufficiently high CPD is glassy for $T^* < 0.12$ [17]. Similarly a monodisperse colloidal suspension is found to have crystalline order for $T^* <$

0.16 [21]. Hence the arguments based on T^* also suggest that the CPD suspension considered here must be solid.

As mentioned earlier, the diffusion of particles is expected to be different in a glass from that in a liquid. Figure 3 shows the behaviour of the MSD up to 1000 MCSs for different CPDs and also their slopes which represent the diffusion constants. It is worth pointing out that MC dynamics lack a strict or rigorous sense of time scale; however, the behaviour of several properties including the MSD as a function of the number of MCSs can still be used to characterize the state of the system [23]. One also recognizes that the true dynamical behaviour of colloids can be obtained using Brownian dynamics [17]. Note that the MSD for 28% CPD exhibits saturation-like behaviour similar to that for a crystalline suspension (zero CPD) but not the linear behaviour expected for a liquid. Linear behaviour for a liquid-like ordered suspension is observed when n_i is varied and is also shown in the figure for comparison. These observations confirm that the disordered state is solid. The long-time slope of the MSD as a function of the number of MCSs is related to the diffusion constant of the particle [23]. Note that the slope of the curve corresponding to 28% CPD quickly reduces to a value close to that corresponding to a zero-CPD system, in contrast with that of a liquid-like ordered suspension (close to the crystal–liquid phase boundary), which remains high. From these results, one can conclude that the suspension at 28% CPD is glass-like.

Having seen that the suspension with 28% CPD exhibits glassy order, it is important to obtain the critical CPD at which the crystalline order is destroyed. The quantities that can be used to identify the C→G transition are the structural parameters obtained from $g(r)$ or $S(Q)$ and also the diffusion. Across the C→G transition, one expects peaks in $S(Q)$ to reduce considerably in height and also to broaden. The first peak in $S(Q)$ for the BCC structure corresponds to the wavevector $Q_0 = (2\pi/a)(110)$, where a is the lattice constant. $S(Q_0)$, which represents the height of the first peak in $S(Q)$, was calculated for all possible orientations of Q_0 (six orientations). S_{max} was then defined as the average of $S(Q_0)$ over all the orientations. 0.8 million configurations were used to obtain good statistics. The S_{max}-value thus obtained is shown in figure 4(a) as a function of the CPD. Note that S_{max} is high in the marginally disordered crystalline state and is rather low, about 5, in the glassy state. S_{max} is expected to decrease across an order–disorder transition of this nature. For comparison, the behaviour of S_{max} as a function of n_i across melting (order–disorder transition) in monodisperse colloids is also shown in figure 4(b). Note that the C→L transition (melting) is also associated with a sudden decrease in S_{max}. It should be pointed out that the largest S_{max} which a liquid-like ordered suspension can have is about 2.85 [6, 16, 21], whereas the disordered state induced by CPD exhibits $S_{max} \simeq 5$, confirming that the disordered state cannot be a liquid. Figure 5 shows the behaviour of another structural parameter g_{min}/g_{max}, i.e. the ratio of the height of the first minimum to that of first maximum of $g(r)$, as a function of CPD. The discontinuous increase in g_{min}/g_{max} across the C→G transition is similar to that reported across the C→L transition [21].

Diffusion in glassy structures is known to be more than that in the corresponding crystalline states [24]. Figure 6 shows the dependence of the MSD at the end of 1000 MCSs on the CPD. Note that the MSD with 26% CPD is significantly higher than that in systems with smaller CPDs. Thus the discontinuous increases in MSD as well as in S_{max} and g_{min}/g_{max} are unambiguously associated with the C→G transition occurring at about 26% CPD. Note from figure 6 that the MSD no longer depends on the CPD,
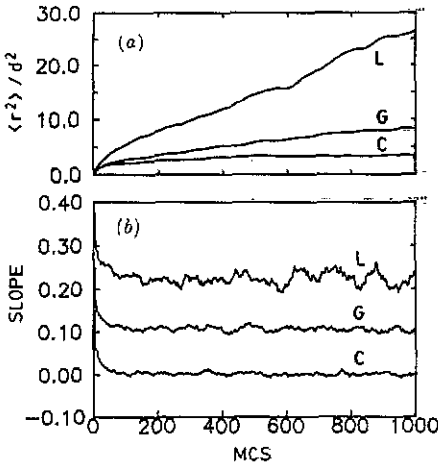
Figure 3. (a) MSD as a function of number of MCSS for 0% CPD (labelled C) and 28% CPD (labelled G). The MSD for a liquid-like ordered suspension (labelled L) for an impurity ion concentration of $1.4 n_p Z_0$ is also shown for comparison. (b) Slopes of the curves shown in (a) representing diffusion constants. The curves G and L are shifted vertically by 0.1 and 0.2, respectively, for clarity. The asymptotic values of slopes are 0.0011(35), 0.0060(55) and 0.024(14) for curves C, G and L, respectively.
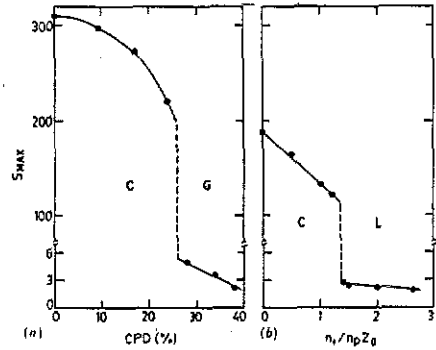
Figure 4. (a) S_{max} as a function of CPD. Note the large decrease in S_{max} of around 26% CPD. (b) The behaviour of S_{max} as a function of n_i (across melting) is also shown for comparison. The lower value of S_{max} at $n_i = 0$ in (b) than that at CPD $= 0$ in (a) is because of the smaller system size ($N = 250$). However, the smaller system size has no influence on the value of S_{max} in disordered states such as glass or liquid. The lines drawn through the points are guides to the eye.

once the state is glassy, implying that the diffusion processes in all the glassy states are alike. It should be mentioned that at the end of 500 MCSS the suspensions with 28% and 32% CPD were earlier found to have an MSD lower than those at higher CPDs. A slowing down of the MC evolution has been recently observed where, close to the critical polydispersity, the system has been found to have a metastable crystalline state lasting over 2×10^6 configurations [25] whereas, for systems away from the critical CPD, the time taken to reach equilibrium is only 9×10^5 configurations. Hence the lower value of MSD reported earlier was due to the metastable crystalline state. The present MC evolutions for sufficiently long times suggest that, once the final equilibrium is reached, the MSD is insensitive to the CPD. It is worth pointing out that $g(r)$ for this glassy state does not show a split second peak, which is often observed in monodisperse and binary glasses [12, 15]. This can be understood as follows. The width of the first and consequently those of subsequent peaks in the $g(r)$ of the charge polydisperse glass are expected to be more than those of a monodisperse glass obtained by quenching. This would cause smearing of the two components of the second peak, resulting in a smooth second peak for CPD glass. Note that even $g_c(r)$, where thermal broadening has been greatly reduced, does not show a split second peak. It is worth mentioning that, in the earlier investigations of the effect of SPD on ordering in colloidal suspensions [7], no attempts have been made to characterize the disordered structure induced by SPD. However, in the present work, on the basis of the behaviour of the diffusion and other parameters, one is able to assign unambiguously the disordered structure to a glassy state.

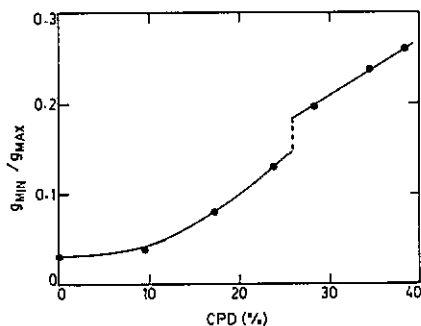As mentioned in the introduction, particles in a dilute aqueous charged colloidal

Figure 5. Structural parameter g_{min}/g_{max} as a function of CPD. The jump at around 26% CPD can be assigned to the order–disorder (C→G) transition. The lines drawn through the points are guides to the eye.
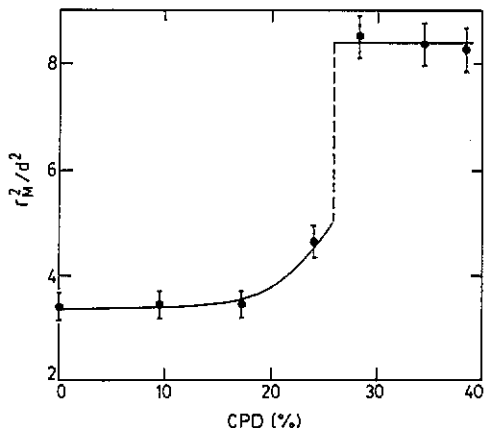

Figure 6. MSD at the end of M ($M = 1000$) MSCs as a function of CPD. The lines drawn through the points are guides to the eye.

suspension can be considered to have an effective hard-sphere diameter arising from strong Coulomb repulsion. The effective hard-sphere diameter of a particle is expected to depend on its charge. Hence, the CPD would lead to a polydispersity of the effective hard-sphere diameters. It is meaningful to estimate the SPD of effective hard-sphere diameters $h(Z)$ for a given CPD and to compare the present results with those reported on size polydisperse systems. $h(Z)$ is estimated in the following manner. The largest r, until which $g(r)$ remains zero in a monodisperse suspension, represents the distance of closest approach for two particles and is taken to be $\overline{h}$ for a particle with charge Z_0. The corresponding diameter $h(Z)$ for a particle with any arbitrary charge Z will depend on Z. Figure 7 schematically shows the distance D_Z of closest approach between particles of charge Z_0 and Z. $h(Z)$ is estimated as $h(Z) = 2(D_Z - \overline{h}/2)$ where the distance D_Z of closest approach between particles of charges Z and Z_0 is obtained by solving $U(D_Z, Z_0, Z) = U(\overline{h}, Z_0, Z_0)$. This is reasonable as the interaction energy between two particles of charge Z and Z_0 at the distance of closest approach is expected to be the same as that for two particles each with charge Z_0, which is about $40k_B T$ at $\overline{h} = 7.15d$. Figure 8 shows $h(Z)$ thus estimated as a function of charge Z. The inset in figure 8 shows the polydispersities ESPD of $h(Z)$ for the CPDs used in the present simulations. Note that the ESPD is significantly lower than the corresponding CPD. Similar results have also been obtained recently in the case of dense charge polydisperse Yukawa fluids [26]. It may be mentioned that, although $h(Z)$ depends on the magnitude of $U(\overline{h}, Z_0, Z_0)$, the ESPD is relatively insensitive to it. The critical CPD of $26 \pm 2\%$ corresponding to the C→G transition corresponds to an ESPD of $17 \pm 1\%$. The critical ESPD value may be compared with that of 11% predicted for hard spheres by Pusey [9] using a simple model. The difference between these two values may be due to the simple procedure to estimate $h(Z)$ used in the present work. Although in any such procedure one tries to estimate h, the presence of the interaction potential beyond h makes the actual system different from a true hard-sphere system. The point that must be emphasized

is that the incompatibility of packing (i.e. size-mismatch frustration) of these effective hard spheres with a wide size distribution leads to glassy order. It may be mentioned that a colloidal liquid with sufficiently high CPD (50%) has been recently shown to undergo a glass transition using Brownian dynamics simulation [17]. The temperature is used as the parameter that drives the transition at $T^* = 0.12$. In this context this study is complementary to the present investigations which probe the structure of the disordered solid at $T^* = 0.04$ as the polydispersity is increased.
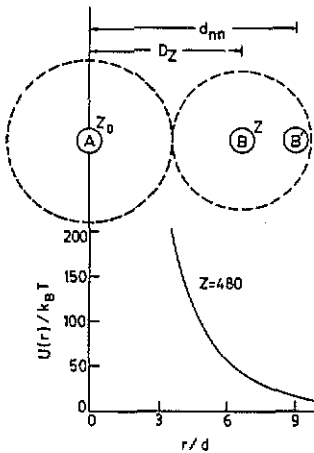

Figure 7. Schematic representation of the distance of closest approach of particles A with charge Z_0 with another particle B with $Z = 480$. The broken circles represent effective hard-sphere diameters. B' represents the equilibrium position of particle B. The lower part of the figure gives the interaction energy between these two particles as a function of interparticle separation.
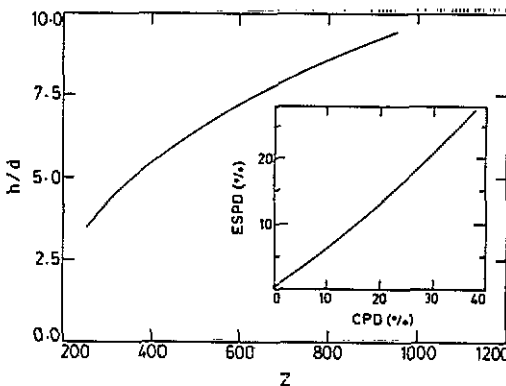

Figure 8. Dependence of the effective hard-sphere diameter h on the charge on the particle. The inset shows the ESPDs for different CPDs.

The critical polydispersity obtained in the present investigation is not universal. It is expected to depend on the strength and the range of interaction which would in turn determine the effective hard-sphere diameter. As the particle concentration, mean

charge and dielectric constant directly determine K and as the size of the particle also appears in the pre-factor of $U(r)$, all these quantities are expected to influence the critical CPD. For example, we have shown that at $n_p = 1.33 \times 10^{13}$ cm^{-3} the critical CPD is about 32% [21]. Apart from the hard-sphere picture of the CPD colloid an alternative way to describe this system will be in terms of a system with random interactions. The interaction energy U between neighbours becomes random because the charges on the particles are random. In this context a CPD colloid would be analogous to a spin glass which also has frustrated spins due to random interactions. It would be of interest to know up to what polydispersity of interaction energy the system can sustain crystalline order [27].

4. Conclusions

To conclude, CPD in colloidal suspensions provides another way of obtaining the glassy state apart from the conventional methods. At low polydispersities the system can be considered to be a marginally disordered crystalline solid. Crystalline order is totally disrupted at about 26% CPD. The behaviour of particle diffusion and structural parameters allows the disordered state to be unambiguously identified as glass like. The estimated polydispersity of the effective hard-sphere diameter is found to be significantly lower than the CPD but comparable with the SPD in hard-sphere systems. Since the SPD and CPD in colloids can be varied easily and rather independently, the present results might stimulate experiments to obtain better understanding of the glassy state.

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