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## LETTER TO THE EDITOR

# Liquid, crystalline and glassy states of binary charged colloidal suspensions

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**Abstract.** The formation of the liquid, crystalline and glassy states in binary mixtures of aqueous suspensions of charged polystyrene spheres of different sizes is investigated. It is shown that on merely mixing the particles, crystalline (a substitutional body-centred cubic) and glassy states are readily formed for a 1 : 1 mixture at appropriate values of the density. These results are in agreement with recent experimental studies. The ease of formation of the crystal and the glassy phases is rationalised by an analysis of the local potential energy profiles calculated using the Hessian (dynamical matrix). It is suggested that the eigenvalues of such a Hessian can be used to define a preferred length scale in any glassy system.

It is well known that when most liquids are cooled sufficiently rapidly below the melting temperature, such that the cooling rate exceeds the crystallisation rate, the system becomes trapped in a metastable glassy state (see [1] for a recent review on glasses). The possibility of forming a glass in certain systems by merely increasing the density at a constant temperature is much less widely appreciated [2]. Lindsay and Chaikin showed that binary mixtures of an aqueous suspension of polystyrene spheres with different diameters inevitably form (Wigner) glasses ([3]; see also [4]). Recently, Pusey and van Megen [5] found that at sufficiently high densities (packing fraction exceeding 0.56) suspensions of almost monodisperse hard-sphere-like colloidal (polymethyl methacrylate) particles undergo a glass transition. These systems are unique, in the sense that glass formation is achieved by simply increasing the concentration of particles, and consequently the mechanism for the transition from the ergodic to the non-ergodic (glassy) state may be different from that for much-studied metallic glasses.

In this Letter, we provide the first molecular dynamics investigation of the crystalline and glassy states in binary mixtures of charged polystyrene colloidal particles. The colloidal particles used in our simulations differ not only as regards the size but also as regards the value of the charge. The most significant result of this work is the observation of the full range of behaviour, liquid → crystal → glass formation, in these systems. When binary mixtures of charged colloidal particles are mixed (for an experimental discussion of the formation of exotic alloys in binary mixtures of colloidal particles, see [6]), several possible phases can result, namely (i) the liquid mixture phase, (ii) the

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formation of a substitutional crystal, (iii) phase separation, (iv) the formation of alloys of the  $AB_2$ ,  $AB_4$  type, and (v) a glassy state. In our study, we find that the binary colloidal suspensions give rise to a liquid mixture and a perfectly ordered body-centred cubic (BCC) crystalline state with the unit cell composed of a small sphere and a large sphere. At higher densities, the system forms a classical Wigner glass. The feature that is perhaps most striking is that the binary mixture of colloidal particles readily becomes a glass when the density is increased and forms an ordered state when the density is decreased (increased) starting from the glassy (liquid) state. Some aspects of the ease of formation of glassy and crystalline states are analysed using the potential energy surface obtained from the eigenvectors of the Hessian.

The binary system of charged polystyrene spheres consists of  $N_1$  spherical particles of radius  $a_1$  and  $N_2$  particles of size  $a_2$ . The interaction potential between the particles is assumed to be of the DLVO form, which has been found to be suitable for describing the properties of electrostatically stabilised polystyrene suspensions [7, 8]. Specifically, the potential  $V_{ij}(r)$  is given by

$$V_{ij}(r) = \frac{Z_i Z_j e^2}{\epsilon r} \left( \frac{e^{qa_i}}{1 + qa_i} \right) \left( \frac{e^{qa_j}}{1 + qa_j} \right) e^{-qr} \quad (i, j = 1, 2) \quad (1)$$

where  $Z_i e$  is the charge on species  $i$ ,  $a_i$  is the corresponding radius,  $r$  is the distance between the particles,  $\epsilon$  is the dielectric constant of water and  $q$  is the inverse Debye screening length,

$$q^2 = \frac{4\pi e^2}{\epsilon k_B T} \sum_i Z_i \rho_i \quad (2)$$

with  $\rho_i$  being the number density of species  $i$ , and  $T$  the temperature. We have assumed that no additional electrolyte has been added to the binary system. Equation (2) follows from charge neutrality. The importance of the geometric factor, given by the terms in the large parentheses in (1), for the colloidal system has been recently stressed [7, 8]. The system is characterised by the composition variable  $X = N_1/N$  (where  $N = N_1 + N_2$ ), the radii of particles  $a_1$  and  $a_2$  and the values of the electronic charge  $Z_1 e$  and  $Z_2 e$ . The thermodynamic condition is specified by the volume of the system,  $V$ , and the temperature  $T$  ( $=298$  K). Notice that in contrast to the usual situation in the canonical ensemble it is the density and not the temperature that is the interesting variable (for a further discussion, see [9]). In our simulations we use volume fraction  $\varphi$  to measure the density where  $\varphi$  is given by  $(4/3V)\pi(N_1 a_1^3 + N_2 a_2^3)$ . The parameters used in the simulations are  $a_1 = 545$  Å,  $a_2 = 1100$  Å,  $Z_1 = 300$ ,  $Z_2 = 600$  which are consistent with the experimental system investigated by Lindsay and Chaikin [3].

In this Letter we present results for a 50:50 mixture. The number of particles used in the simulation is 1024. The liquid configurations were generated from an initial lattice and by subsequent long equilibration times of about  $10^4 \Delta t$ , where  $\Delta t$  ranged from  $0.005 \tau$  to  $0.01 \tau$ , with  $\tau = (\beta m a^2)^{1/2}$  and  $a = (a_1 + a_2)/2$  (where  $m$  is the mass of the particles). Other configurations were generated by expanding or contracting the density. Details of the molecular dynamics calculations can be found elsewhere [7, 10].

The criterion used for determining the state of the binary mixture is the following. For all the volume fractions considered, we computed several correlation functions, and the state of the system was determined by using a combination of the pair correlation function and the mean square displacement (MSD). Thus, for a liquid configuration one expects short-range order in  $g(r)$  and the MSD should vary linearly with time whereas in

a glass one expects only short-range (or intermediate) order and a saturation in the value of MSD. A crystal, on the other hand, should exhibit long-range order in  $g(r)$  and the MSD should tend to a constant as  $t \rightarrow \infty$ . Using this criterion, we find that a mixture with a composition  $X = 0.5$  is a liquid when the volume fraction is less than about 0.0075. When  $\varphi$  is increased to 0.01 the system spontaneously freezes into a completely ordered state. The crystalline  $g(r)$  corresponds to that of a BCC lattice. On decomposing the total  $g(r)$  into partial radial distributions corresponding to the two differently sized particles, it becomes clear that the BCC lattice is made up of two interpenetrating simple cubic lattices. The two simple cubic lattices are made up of particles of just one kind. Thus, the unit cell for this BCC structure consists of one particle of each species. In the light scattering experiments, only after a long time was the formation of small crystallites detected. This may be due to the inherent polydispersity in the sample which prevents nucleation from occurring. For  $\varphi > 0.01$ , the sample forms a glass with the characteristics described above. If the density of the glass is decreased to about 0.01 we find that the system spontaneously arranges itself into the crystalline configuration, suggesting that nucleation from the glassy state is easily achieved.

In order to test the ease of formation of the ordered state further, the volume fraction at which spontaneous crystallisation takes place ( $\varphi = 0.01$ ) was arrived at in several distinct ways. Firstly, the crystalline state was formed by increasing the volume fraction of the liquid from  $\varphi = 0.005$  to  $\varphi = 0.01$ . In an alternative way, a glassy state was prepared at  $\varphi = 0.100$ . The initial configuration for this state ( $\varphi = 0.100$ ) was obtained from a well equilibrated homogeneous sample consisting of monodisperse colloidal particles with the radius equal to  $a_1$ . The resulting state for the monodisperse system was found to be a BCC crystal. The initial configuration for the glassy state was obtained by randomly assigning the larger diameter to one half of the particles. The system was then aged and this resulted in the formation of a glassy state. The volume fraction was subsequently decreased to  $\varphi = 0.05$  where the state of the system remained unchanged. Finally,  $\varphi$  was decreased to 0.01 and the crystalline (BCC) state that resulted was identical to that obtained from the first path. In an entirely different exercise, an initial configuration for  $\varphi = 0.01$  was prepared with the top of the box containing the smaller particles and the bottom half of the box containing the larger particles. It was found that upon equilibrating, an ordered substitutional BCC crystal resulted, implying that barriers to nucleation in these systems are small. The formation of the stable ordered phase from completely different initial conditions suggests that the thermodynamically stable state is indeed a crystal. We disagree with recent claims that the ground state of charged binary colloidal polystyrene spheres may be a glass [4]. The crystallisation time increases considerably as  $\varphi$  increases and it is probably for this reason that these authors did not observe the growth of crystallites in their samples.

For a fuller illustration of the 'reaction pathway' leading to the ready formation of the crystalline phase from both the liquid and the glassy phase, the topology of the potential energy hypersurface was investigated by using the properties of the Hessian [11–13]. We have previously argued that dynamical processes that dominate relaxation in undercooled liquids and glasses are local, involving only a few particles [14]. Thus, we expect that the transition from one metastable well to another metastable (or stable) state will take place along an optimal pathway involving the coordinates of the particles involved in the activation process. The optimal pathway can be characterised by a complicated reaction coordinate,  $Q$ . In general, for many-body systems the functional form of  $Q$  (or even its existence) is hard to determine but it is obvious that the collective coordinate  $Q$  should be a function of the positions of the particles involved in the local

dynamics. While the precise form of  $Q$  is difficult to determine, a natural set of  $Q$ -values can be obtained by considering the eigenvectors of the instantaneous dynamical matrix, whose elements are

$$D_{\alpha\beta} = \partial^2 \varphi / \partial x_\alpha \partial x_\beta \quad (3)$$

where  $\varphi$  is the total potential energy of the  $M$ -particle subsystem specifying the local event.

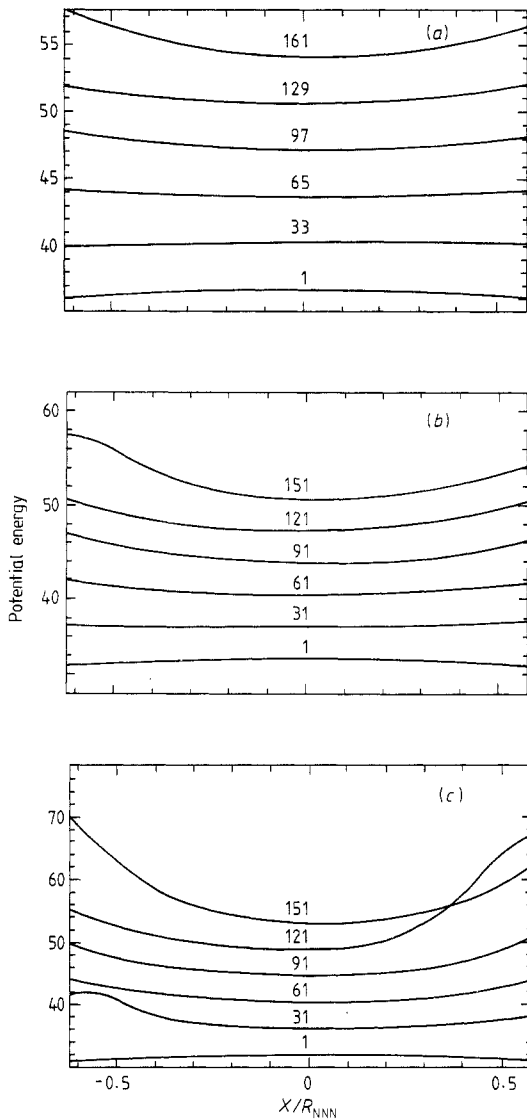
In the cases considered here, the sections of the potential energy hypersurface were constructed from  $\mathbf{D}$  as follows. Given a well equilibrated configuration, an arbitrary particle is chosen. The first- and second-nearest neighbours of that particle are located. The second-neighbour distance is obtained by specifying a cut-off distance that roughly corresponds to the second minimum in the radial distribution function. For this cluster of particles, the dynamical matrix is computed using (3) and the eigenvalues and the eigenvectors of  $\mathbf{D}$  are obtained by diagonalisation. This gives  $3M$  eigenvalues,  $\omega_k^2$ , and the same number of eigenvectors,  $e_k$ . The possible cooperative local motion of the chosen particles is assumed to proceed along the eigenvector  $e_k$ , although such a decomposition is hardly unique. For a specified eigenvalue, the  $M$  particles are displaced along the corresponding eigenvector. This entails displacing each particle by a fraction of the second-nearest-neighbour distance:

$$\mathbf{X}'_k = \mathbf{X}_k + \delta R_{\text{NNN}} e_k \quad (4)$$

where  $\mathbf{X}'_k$  is the displaced position,  $\mathbf{X}_i$  is the original coordinate,  $\delta$  is a number,  $0 \leq \delta \leq 1$ , and  $R_{\text{NNN}}$  is the second-nearest-neighbour distance. The total potential energy,  $\varphi$ , is calculated using the coordinates,  $\mathbf{X}'_k$  ( $k = 1, 2, 3, \dots, M$ ).

We first discuss some characteristics of the eigenvalues and their distributions,  $g(\omega)$ . The eigenvalues of the Hessian were computed for three values of the volume fraction,  $\varphi = 0.001$  (liquid state, L)  $\varphi = 0.01$  (crystalline state, C) and  $\varphi = 0.1$  (glassy state, G). The percentage of negative eigenvalues for the L, C, G states was found to be approximately 11, 4, 3, respectively. The higher value in the crystal is an indication that a microcluster formed from a crystal can be metastable with respect to a glassy cluster or amorphon. It is interesting to note that the percentage of negative eigenvalues in the liquid state for the colloidal system is considerably less than that found in (almost) Lennard-Jones systems at and above the melting temperature [15].

The potential energy profiles for a few selected eigenvalues for the L, C and G states are displayed in figures 1(a), 1(b) and 1(c), respectively. The value of cut-off used to define a cluster in the sample was  $2.44 a_s$  where  $a_s = (N/V)^{1/3}$ . The value of  $M$  for this choice of cut-off was 65, 61, 60 for the L, C, G states, respectively. The figure shows several interesting features. In both the liquid and the crystalline states we have shown the unstable modes, corresponding to the negative eigenvalues. The curvature near the equilibrium position for the unstable modes is smallest in the liquid state. The minimum in the potential energy profile in both the crystalline and the glassy state almost always occurs at zero which is defined to be the equilibrium position. In the liquid state, there appear to be eigenmodes that are not in equilibrium (defined to be the instantaneous location of the particles in a typical configuration). In the colloidal systems, the total energy is dominated by the potential energy term. Thus, even in the liquid state it is the optimisation of the potential energy that is relevant and it is for this reason that the minimum in most of the potential energy profiles appears at zero. Such modes also exist in the crystalline and glassy states but they are not as frequent. All the profiles clearly indicate that the potential energy surfaces are highly anharmonic. Finally, one notices



**Figure 1.** (a) Potential energy profiles for arbitrarily selected eigenmodes with the number indicating the mode number, as functions of the reduced distance in the direction of the eigenvector. The energy is measured in units of  $k_B T$ . This figure corresponds to  $\varphi = 0.001$ , a liquid state.  $M = 65$ . The eigenstates of the six states shown correspond to squared frequencies of  $-2.5, -0.3, 1.5, 3.9, 5.6$ , respectively, in increasing order. (b) As (a), but for the crystalline state, with  $\varphi = 0.01$ .  $M = 61$ . The eigenvalues of the modes shown correspond to squared frequencies of  $-42.1, 25.1, 41.0, 69.9, 92.2, 144.6$ , respectively in increasing order. (c) As (a), but for the glassy state, with  $\varphi = 0.1$ .  $M = 60$ . The eigenvalues of the modes shown correspond to squared frequencies of  $-1185.8, 1193.1, 1908.3, 2863.8, 4105.8, 6647.2$ , respectively, in increasing order.

that the profiles in the glassy state show barriers (whose height exceeds  $k_B T$ ) indicating that the motion along those specified collective coordinates involves activated transitions. It is tempting to suggest that motion along these eigenvectors corresponds to diffusion paths in glasses.

The technique outlined above may be used to infer the existence of a preferred length scale in glasses. Such a notion has been recently used to estimate the number of particles involved in regions where particle motions are highly correlated in a variety of glass-forming materials [16]. As has been discussed above, we find that the number of unstable modes in the glassy state is less than that in the crystal, if one considers particles within a specified cut-off distance from a tagged particle. Clearly, if one looks at a large enough length scale then the percentage of unstable modes in a crystal has to be less than that

of the glass. Thus, a preferred length scale in glasses,  $\xi$ , can be defined as the maximum distance such that the percentage of unstable modes of the Hessian obtained by considering the particles within  $\xi$  is equal to the percentage of negative eigenvalues in the crystalline state for particles within  $\xi$ . Adopting this definition, we estimate  $\xi$ , which clearly depends on the density, to be between  $2\rho^{-1/3}$  and  $3\rho^{-1/3}$  for  $\varphi = 0.1$ . There are roughly 100 particles in this length scale. This number is not very different from the estimates made for glassy states in a binary mixture of soft spheres [17].

We also carried out a preliminary analysis of the stability of the crystal state by looking for the largest deviation,  $\delta\varphi$ , around the crystalline volume fraction of  $\varphi = 0.01$  that destroys the long-range order. The approximate bound we have obtained is  $|\delta\varphi| \approx 0.0005$ . Thus, a five per cent decrease in the volume fraction from  $\varphi = 0.01$  produces a liquid. A detailed analysis of the stability of colloidal crystals and glasses will be given elsewhere [10].

Finally, we note that the results obtained here are in agreement with the experimental study of Lindsay and Chaikin [3]. These authors also find the formation of liquid and glassy states by preparing the sample in many different ways. They made the suggestion (based on a preliminary analysis) that the ordered state indicates the presence of both sizes of sphere. Our simulations clearly show the formation of such an ordered BCC state. We have also examined the phases that result for other values of the compositions. The formation of a crystalline state for a certain range of  $X$  (containing mostly the small spheres) is found to be more difficult [10].

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