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Signature of glass transition in a strongly correlated 2D liquid

Haimanti Chakrabarti¹ and Barnana Pal²

¹ Department of Physics, Bidhannagar College, EB-2, Bidhannagar, Kolkata-700 064, India

² Saha Institute of Nuclear Physics, 1/AF, Bidhannagar, Kolkata-700 064, India

E-mail: chakhmt@yahoo.com and barnana.pal@saha.ac.in

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Abstract

A realistic model to study the properties of an aqueous electrolyte surface has been developed. The complex liquid surface consisting of a large number of interacting particles, ions and dipoles, is modelled using a Monte Carlo technique considering grand canonical sampling. The possible interactions existing in the system are charge–charge, charge–dipole, charge–quadrupole and dipole–dipole. The concentration dependence of the diffusion coefficient suggests a first order phase transition (structural transition), while its temperature dependence indicates the existence of a second order phase transition. A critical analysis of the effect of decreasing temperature on the samples with added cations to limit motion of the particles in the surface reveals an interesting feature—a signature of glass transition.

1. Introduction

A liquid surface always poses many interesting questions because of its wide variety of physical properties compared to those in the bulk. For example, the surface tension of a salt solution increases considerably due to a depletion zone of salt ions close to the free surface [1]. There has been an explosion of interest [2] in studying the properties of 2D aqueous electrolytes in various fields of colloidal, electrochemical and biological science. Recently interfacial and surface effects have received attention primarily in the context of ionic systems due to their technological relevance to nuclear medicine and nanoelectronics. To be more precise, interest increased as soon as the transport mechanism in 2D aqueous electrolytes was practically realized by membranes consisting of cationic and anionic lipids and surfactants. It is also becoming clear that the influence of fluctuation effects, such as those captured with the Debye–Hückel theory on the interaction between the charges, will play a role in a variety of biological phenomena such as absorption of DNA on charged membranes. Moreover the interaction between test charges at the surface of a 2D salt solution (the uppermost layers of a salt solution or a thin film) has also been shown to decay algebraically. All this information gives rise to

many interesting questions. Several avenues of study are germane to a thorough understanding of highly correlated 2D systems.

It seems quite difficult to tackle a highly correlated 2D liquid system composed of innumerable particles, ions and water molecules. Moreover, there is still no generally agreed structural model of such system. Even if some techniques [3] that have already been developed for 3D liquid systems [4] can be extended to explore the behaviour of such 2D liquid systems, the experimental results suffer from a lack of theoretical support. The available theory is limited to the phenomenological continuum approach and fails to characterize the complexity of the liquid system. One of the simplest non-primitive models is the ion–dipole model [5], consisting of hard spheres having equal diameters with charges embedded on them in a sea of point dipoles. To get an insight into the structure as well as the dynamical properties of such systems, diffusion can be chosen as a tool. But devising experiments to probe the transport mechanism in a highly correlated 2D system is not straightforward. Computer simulations, being neither experiment nor theory, can take over the task of both. Moreover the real system and the physical situation can be metamorphosed gradually from the ambient condition of a very primitive system. Thus for complicated liquid systems like 2D aqueous electrolytes which have so far remained analytically intractable, computer simulations can take the role of a theoretical approach and throw new light on the analysis of experimental results. In this work an extensive study of the concentration and temperature dependence of the diffusion coefficient for both ions and water molecules in the surface of an aqueous electrolyte has been made. Surface diffusion coefficients are obtained by Monte Carlo simulations, because when a general model of network-forming fluids is solved without the use of such approximate techniques pure fluid–liquid equilibrium occurs.

2. Methodology

In the present study diffusion of charged particles in 2D aqueous electrolytes has been studied using a non-primitive method in which the solvent is modelled as molecules rather than a continuum. A standard Metropolis algorithm has been used to simulate the system. The particles are initially placed randomly at the lattice sites of a 10×10 square lattice having interatomic spacing of length 10×10^{-10} m. Such a choice of lattice size is made to keep parity with the existing simulation works done for 3D systems for which the system size does not exceed $10 \times 10 \times 10$. This helps to analyse critically how the diffusion pattern changes in a similar system with the change in dimension only. These particles, when considered for a Monte Carlo move, are allowed to take any position and any orientation inside this 2D space to generate liquid state configurations. Periodic boundary conditions are used to minimize the size effect. For the initial stage two ions, one positive and one negative, and n dipoles, representing water molecules, are placed randomly at the lattice sites. Electrolytes of different concentrations (number density) are obtained by varying n . Only nearest neighbour interactions are considered initially. The effective interactions existing in the system considered are charge–charge, charge–dipole and dipole–dipole. 10^5 Monte Carlo steps (MCS) per particle are allowed to reach the equilibrium configuration. The state parameters used in the simulation procedure are listed in table 1.

The diffusion coefficient of individual specific particle is defined as

$$D = \frac{1}{2d} \lim_{t \rightarrow \infty} \frac{1}{t} \left\langle \frac{1}{N} \sum_{i=1}^N |\mathbf{r}_i(t) - \mathbf{r}_i(0)|^2 \right\rangle = \frac{1}{d} \int_0^\infty \left\langle \frac{1}{N} \sum_{i=1}^N \mathbf{v}_i(t) \cdot \mathbf{v}_i(0) \right\rangle dt$$

where $d = 2$ is the dimension of the system and $\mathbf{r}_i(t)$ is the position vector of particle ‘ i ’ at time t and $\mathbf{v}_i(t)$ its corresponding velocity. The quantity $\phi(t) \equiv \langle \sum \mathbf{v}_i(t) \cdot \mathbf{v}_i(0) \rangle$ is

Table 1. Parameters used in simulation (primitive model).

Molecular properties			
Charge of ion	1.6×10^{-19} C		
Dipole moment of solvent	1.8 debye		
Configuration of sampling parameters			
Maximum displacement per configuration	0.05 times box length		
Maximum rotation of dipole per configuration	4.5° in θ		
Concentration			
No of ions	2	2	2
No of dipoles	40	53	66
Total no of particles	42	55	68

the velocity autocorrelation function associated with the specific particle. In evaluating the diffusion coefficients during the simulations one may also employ the memory expansion method [7]. However, similar results are obtained within the limits of the present method. This embryonic model offers signatures of quite interesting results and requires modifications for the real physical situation. So different modifications have been made to fine tune the program. Apart from the interaction terms considered earlier in the primitive model [9], another term is included in the interaction potential—the charge–quadrupole interaction—since at finite electrolyte concentration the interfacial charges are subject to a repulsive interaction that varies with the inverse third power of their distance $V \propto |\mathbf{r}_{ij}|^{-3}$ [9]. The possible interactions are of the form:

$$\begin{aligned} \text{charge–charge} &= \phi_{c.c.}(\mathbf{r}_{ij}) = q_i q_j (|\mathbf{r}_{ij}|)^{-1}, \\ \text{charge–dipole} &= \Phi_{c.d.}(\mathbf{r}_{ij}) = -q_i \boldsymbol{\mu}_j \cdot \nabla (|\mathbf{r}_{ij}|)^{-1}, \\ \text{dipole–dipole} &= \Phi_{d.d.}(\mathbf{r}_{ij}) = -(\boldsymbol{\mu}_i \cdot \nabla)(\boldsymbol{\mu}_j \cdot \nabla)(|\mathbf{r}_{ij}|)^{-1}, \\ \text{charge–quadrupole} &= \Phi_{c.q.}(\mathbf{r}_{ij}) = -q_i \Theta : \nabla \nabla (|\mathbf{r}_{ij}|)^{-1}, \end{aligned}$$

where r_{ij} is the distance between q_i and q_j , the charges at the i th and j th sites, and the double dot is the Chapman–Cowling notation used to represent the inner product of two tensors.

The sampling option used for a many-ion system is the grand canonical one, since our chosen surface is the uppermost part of a bulk system separated only by a hypothetical perforated wall through which it can exchange both energy and number of particles. Added to it, as the particles are at liberty to move randomly inside the lattice during simulation, random moves are conducted as a Markov process to generate a sequence of configurations. There are four types of moves in the simulation—displacement, rotation, creation and deletion. The last two types are chosen because in the course of random motions particles from the bulk may come up to the surface, i.e. a particle that was once not on the surface may virtually be created on the surface at another instant or a particle that was once at the surface may go to the bulk; thus a particle that was once at the surface may not remain at the surface at the other instant. The state parameters newly introduced in the simulation procedure for this modified model are listed in the table 2. The values of μ and q correspond to the dipole moment of water and the charge of the monovalent ion.

To reach equilibrium configuration at least 10^5 MCS per particle are allowed. This fixation of the number of MCS was decided via a process which shows that fluctuations in $\langle(\Delta r)^2\rangle$ decrease gradually and attain almost a constant value, at least after 10^5 steps. Due to the long range of the Coulomb interaction, simulation of charged and polar fluids has always been a difficult task and at the same time finite size effects become a serious problem. Here, Ewald summation [10] is performed to cope with the situation. It mainly minimizes the artefacts

Table 2. Parameters used in simulation (modified model).

Molecular properties	
Diameter of ion	3.0×10^{-10} m
Configuration of sampling parameters	
Real space cut-off distance R_{cut}	$5\sigma, 7\sigma, 7.5\sigma, 10\sigma$
Ewald sum parameter	
Convergence parameter	2.8
K_{max} cut-off in real space	3.0
State parameters	
Reduced density	Varied from 0.6
Reduced charge q	8, 13.6
Simulation conditions	
Number of ions	Varied from 2 to 38 depending on the packing density P
Number of dipoles	Varied from 20 to 68 depending on the packing density P

created by use of a cut-off in a small system. Incorporating all these modifications, 2D aqueous electrolytes with ' m ' positively charged ions, ' m ' negatively charged ions and ' n ' point dipoles are configured and simulated under various physical conditions. A new parameter P , the packing density, is defined to parameterize the pressure in the hypothetical lattice in terms of the total number of particles occupying the lattice points with respect to the total number of lattice points [$P = (m + n)/100$]. The diffusion of both positive and negative charges has been calculated separately at different temperatures T ranging from 10^{-6} to 10^6 eV for a wide range of packing densities P by varying ion number, dipole number and number density of ions. To obtain high quality statistics five to eight independent simulations for each state point were performed where there were appreciable fluctuations, but for coherent data the average is taken over three configurations. The standard deviations estimated for these data are found to lie within the confidence level of the data points shown in the figures.

Here it is worth mentioning that the maximum occupancy of the chosen system is 80% (which is filled with both ions and dipoles), the remainder being cavities. Knowledge of the distribution of these cavities is very important since the density of liquid water can be calculated. Using a random number generator we satisfactorily choose cavities in the periodic box containing ' n ' water molecules. Due to thermal motions these cavities fluctuate and collapse quickly, generating newer ones of different shapes. However, for a few configurations simulations have been carried out for $P = 0.8$, but they do not reveal any new information compared to those obtained for $P = 0.7$ for low ' m ' values. For high ' m ' values the $m:n$ ratio is much greater than 1 and does not represent any real physical system of current interest.

3. Results and discussion

Initially surface diffusion coefficients (D) of a positive charge have been calculated with the embryonic model with the state parameters listed in table 1 over the temperature range from 10^{-6} to 10^6 eV for a two-ion system with 40, 53 and 66 dipoles. During this calculation the minimum number of MCS was chosen as 10^5 . This choice was made as a result of a systematic study of the variation of the average of the square of the displacements $\langle(\Delta r)^2\rangle$ from their previous positions with the number of Monte Carlo steps (N) for water at different configurations corresponding to different densities. Figure 1 gives the variation

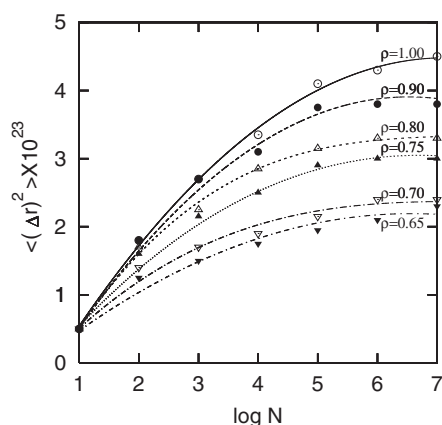


Figure 1. Variation of the average square displacements $\langle(\Delta r)^2\rangle$ of water molecules in m^2 with Monte Carlo steps N (on a logarithmic scale) for different particle densities ρ in m^{-2} .

of $\langle(\Delta r)^2\rangle$ for water molecules as function of $\log N$ at different densities (ρ). $\langle(\Delta r)^2\rangle$ is found to increase with increasing N , the rate of increase being higher for higher densities. After $N = 10^5$ an almost steady value is attained by $\langle(\Delta r)^2\rangle$ for all the densities except $\rho = 1.00$. The situation for $\rho = 1.00$ should be given special consideration since it corresponds to the characteristic density of water at which anomalous properties show their highest manifestation. Moreover, with the increase of temperature water shows regularity in its characteristic properties, including lowering of density, which is also reflected in the graph at or after 10^5 MCS. So the choice of at least 10^5 MCS to reach the equilibrium configuration is justifiable. A thorough examination of the variations of the diffusion coefficient studied with a starting configuration of two ions and 28 dipoles reveals that the transition temperature T_g varies with change in the number density of particles.

Figure 2(a) presents the variation of the diffusion coefficient D measured in $\text{m}^2 \text{s}^{-1}$ with temperature T measured in eV, both on a logarithmic scale in the temperature range 10^{-6} to 10^{+6} . It is clear from figure 2(a) that the temperature dependence of the diffusion coefficient shows the existence of a critical temperature T_g , on two sides of which there is a drastic change in the order of the diffusion coefficient. Moreover, the variations in the D values at high temperature are than those in the low temperature region. The detailed behaviour in the low temperature region is shown in figure 2(b). The $\log T$ versus $\log D$ curve shows the following interesting features:

- (1) The surface diffusion coefficients for all the three systems are more or less same in the range above T_g .
- (2) Figure 2(b) shows that if the temperature is decreased below T_g , D starts increasing up to a certain temperature T_p and then again decreases. T_p shifts towards zero temperature with the decrease in the number density of water molecules, as is evident from the curves for the two systems consisting of 66 and 53 water molecules. T_p is not observable in the figure for the system having 40 water molecules, but from the trend of the curves it may be anticipated that T_p for this case lies below 10^{-6} eV.

Figure 3 represents the variation of the diffusion coefficient for a two-ion system (with 66 dipoles) in the same temperature range for both primitive [11] and modified models. Table 3 presents a comparative study of these two sets of data. It shows that both the models display

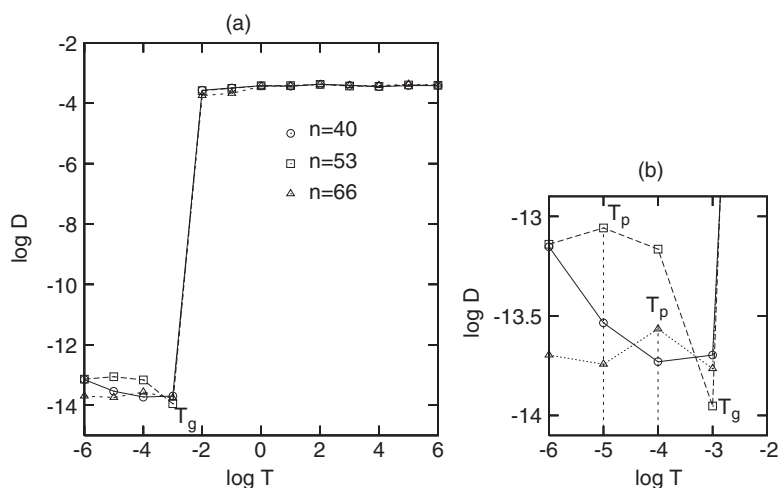


Figure 2. (a) Variation of the surface diffusion coefficient D in $\text{m}^2 \text{s}^{-1}$ with temperature T in eV (both on a logarithmic scale) for dipole number $n = 40, 53$ and 66 with one positive and one negative ion. The low temperature region is shown in (b) at an enlarged scale.

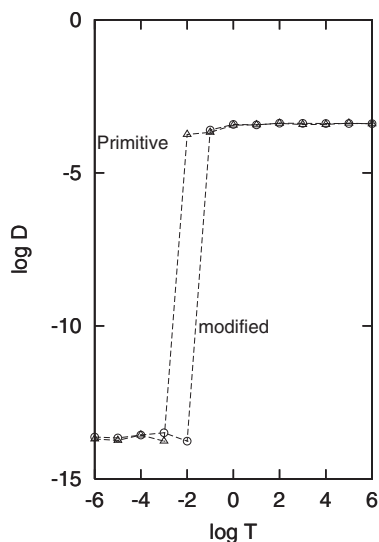


Figure 3. Variation of the surface diffusion coefficient D in $\text{m}^2 \text{s}^{-1}$ with temperature T in eV (both on a logarithmic scale) with parameters of the primitive and modified models.

the same basic characteristics, but in the second one the transition region is shifted towards a lower temperature.

The effect of changing the ion number density on T_g for different P at constant dipole number density is presented in figure 4, while figure 5 delineates the dependence of the same parameter on variation of dipole number density for different P at constant ion number density. The spurious changes in diffusion data obtained at some particular situations can be rationalized by the conjecture of site blocking. The variations of T_g with ion number density and dipole number density are presented in figure 6. It has been observed that the values of T_g obtained

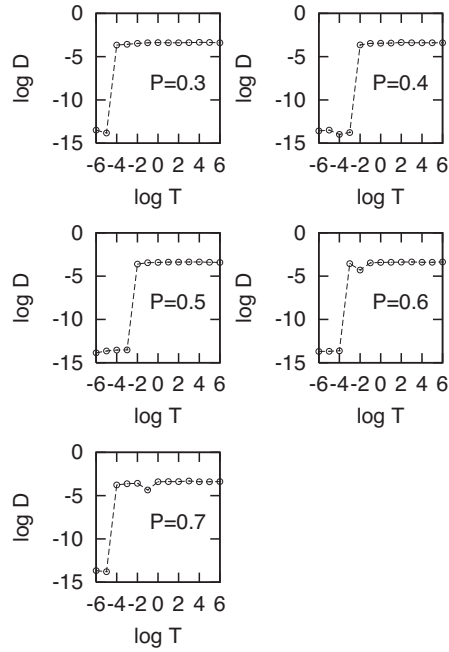


Figure 4. Variation of the surface diffusion coefficient D in $\text{m}^2 \text{s}^{-1}$ with temperature T in eV (both on a logarithmic scale) for different packing densities $P = 0.3, 0.4, 0.5, 0.6$ and 0.7 . Different packing densities are obtained by varying the number of ions, keeping the dipole number density fixed at 28×10^{20} particles m^{-2} .

Table 3. Comparative values for the transition temperatures.

System under	$\log T_c$	$\log T_p$	General trend	Remarks
Embryonic model	-2.3	-4.0	All the characteristics are the same excepting that the values have slightly changed	The embryonic model and the modified model are metamorphosed successfully
Modified model	-2.0	-5.0		

from the comparatively simpler model also fall on this straight line, suggesting a coherence between the two models. For variation of dipole number density, T_g decreases linearly with the increase of P , while for variation of ion number density T_g increases linearly with the increase of P . Under the same physical conditions, if dipoles are added to an ion-dipole network the structure becomes stronger but as soon as ions are added the chance of rupture of the network increases. So the reverse tendency is consistent with the network-strengthening capacity of dipoles and the network-rupturing tendency of ions. The two linear curves intersect at a packing density of 0.5, illustrating almost the same size effect for the two.

All these studies point to the fact that D values show a sharp change at $T = T_g$, which points to the ultra high viscosity of the system and is supported by the similar signature of anomalous rise of viscosity accompanied by a depression in diffusion data for similar 3D systems [12]. Moreover, such ultra viscosity has already been reported [13] for bulk water at atmospheric pressure on cooling. Actually, aqueous systems close to freezing point have a local structure similar to the solid; however, in the equilibrium configurations there are some concentrations of dislocations which cannot move to the surface under the influence of an

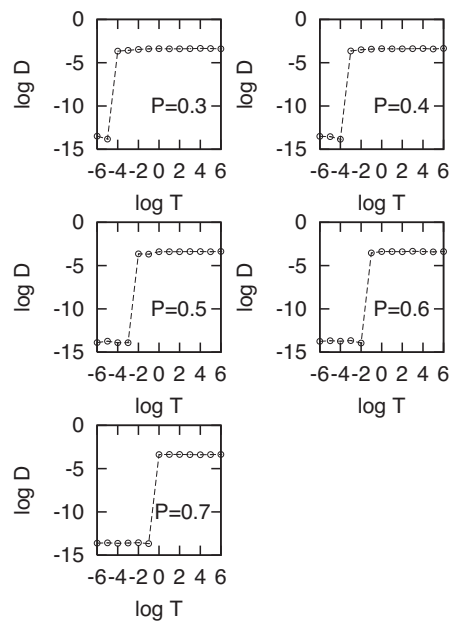


Figure 5. Variation of the surface diffusion coefficient D in $\text{m}^2 \text{s}^{-1}$ with temperature T in eV (both on a logarithmic scale) for different packing densities $P = 0.3, 0.4, 0.5, 0.6$ and 0.7 . Different packing densities are obtained by varying the number of dipoles, keeping the ion number density fixed at $2 \times 10^{20} \text{m}^{-2}$.

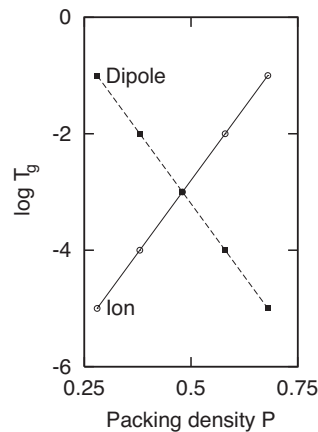


Figure 6. Variation of T_g in eV (on a logarithmic scale) with packing density P at fixed ion number density $2 \times 10^{20} \text{m}^{-2}$ and dipole number density $28 \times 10^{20} \text{m}^{-2}$.

arbitrarily small shearing stress and produce viscous flow [14], whereas in the solid state there is no free dislocation in equilibrium and so the system is rigid. It has been found that the spectrum of data obtained can be clarified and better understood by comparing them with the diffusion coefficients typically expressed in the Arrhenius form, $D = D_0 \exp(-E_{\text{diff}}/kT) \text{cm}^2 \text{s}^{-1}$, where E_{diff} is the activation energy and D_0 is the diffusion coefficient at absolute zero. So the motion in a 2D system is more restricted compared to that in a 3D system of the same

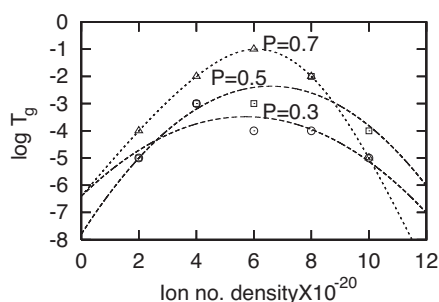


Figure 7. Variation of T_g in eV (on a logarithmic scale) with ion number density for packing density $P = 0.3, 0.5$ and 0.7 .

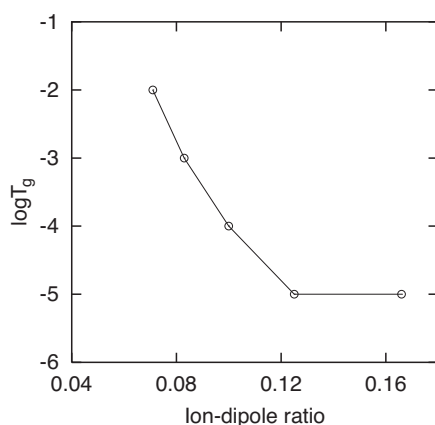


Figure 8. Variation of the transition temperature T_g in eV (on a logarithmic scale) with ion–dipole ratio.

sample. All these facts point to the occurrence of a glassy state at or in the neighbourhood of T_g and the transition occurring at T_g is a glass transition, typically produced from the liquid state by continuous cooling.

Moreover a critical analysis of the variation of transition temperature with different ion number densities at different packing densities reveals that as the number density of particles increases the transition region gets more sharply defined. This is shown in figure 7. The transition starts showing a maximum value instead of a plateau like region.

The dependence of the transition temperature T_g on the ion–dipole ratio is depicted in figure 8. It is interesting to note that this transition temperature decreases gradually with increase in the ion–dipole ratio to attain a fixed value of 10^{-5} when the ion–dipole ratio reaches a value of 1:8.

In contrast to the density dependence, the temperature dependence of the network is very small. Actually a detailed understanding of the influence of temperature should presumably be best described by thermal excitation within the topological framework determined by the density. For this a variation of diffusion coefficients obtained from a Monte Carlo study with different packing densities at different ion–water number densities (1:1 to 1:7) over the same temperature range reveals interesting features regarding phase transition that are worth pursuing. To be more specific, the experimental data are suggesting a structural transition—the

system separates into two coexisting phases which are in dynamic equilibrium, and the particles are expected to exchange between phases with time. To identify the structure and the ion–water ratio we separate water molecules into two groups—low density and high density—according to the number of neighbours within 0.35 nm of each molecule averaged over 200 ps. The choice of 0.35 nm and 200 ps has been made because

- (1) r_{\min} commonly used to define the 1st neighbours shell is the distance coincident with the first minimum in the O–O radial distribution function $g(r)$ which is approximately 0.35 nm.
- (2) During 200 ps particles diffuse by less than one molecular diameter—a distance much smaller than the characteristic size of each of the two coexisting phase.

For a better understanding, a study of the effect of decreasing temperature on the sample with added cations and anions to limit their motion in the structure has been carried out. Isolated dislocations cannot occur at low temperature in a large system except near the boundary, because their energy increases logarithmically with the size of the system. In general the interaction of liquids and supercooled liquids with solid surfaces tends to slow down the molecular motion, but if it is confined within the boundary of ions the glass transition temperature is attained and thus speeds up the dynamics at least at temperatures close to T_g . Hence there is competition between the confinement and the surface effect. So, depending on the temperature and position in the boundary and the nature of surface interaction, the relaxational motion will either slow down or be bogged down.

However, a thorough analysis of the obtained data requires information regarding the short time dynamics and structures of interlayer water molecules in aqueous electrolytes. With a view to characterizing the different transitions and understanding the dynamics of the 2D aqueous electrolytes in the glassy state, a freezing criterion based on the structural properties of 2D dense fluids using L – J potential is being investigated.

A flavour of the way in which structural changes influence the dynamics of metastable water can be obtained from figure 1. For calculation of the density the maximum occupancy in the hypothetical lattice is noted, the remainder is cavities. Knowledge of the distribution of these cavities is very important since the density of liquid water can be calculated from this using a random number generator. Due to thermal motion, such cavities fluctuate and collapse quickly. It appears that density has a major influence on the topology of a hydrogen-bonded network, when the ion–water ratio remains the same. In this situation as density of water increases the transition temperature changes, showing an anomalous variation which can only be explained by the coexistence of high density and low density water. With decrease in density, the local order becomes more tetrahedral, the number of nearest neighbours decreases to four and local arrangements with more than four hydrogen bonds disappear. Moreover the variable interparticle distance suggests that the particles do not experience consistently balanced attractive and repulsive forces at the interfaces that would lead to ordered arrays.

In addition to this the agreement between the network statistics of the liquid and the result based on the topology of ice becomes very close. However, that is not conclusive and does not mean that the real topology of crystalline ice is obtained. Therefore these structural changes are best described by an approach to glassy state ice.

When the packing density is varied from 0.3 to 0.7 to achieve the density variation, fixing attention at a particular temperature below $\log T = -1$, it is seen for all the systems that the magnitude of the diffusion coefficient changes drastically with packing density. This observation offers the possibility of the occurrence of a drastic change in the nature of diffusional motion, and thereby understanding the mechanisms governing the single particle motion in the light of the switching of hydrogen bonds rather than rupture has to be considered.

Actually when a molecule is displaced its hydrogen bonds with some neighbours become weaker and those with other neighbours become stronger so that none of the hydrogens is at any moment outside the influence of hydrogen-bond forces, as can be deduced from intramolecular (OH) oscillator frequencies measured by IR spectra. This switching is actually possible if the system contains a certain number of hydrogen bonds. Decreasing the density means lowering the number of neighbours and approaching a perfect tetrahedral local order. The possible number of bonds, in particular the number of bifurcated bonds, is then reduced, leading to the observed decrease in mobility. This can be studied rigorously by varying ion–dipole ratio values. It is worth mentioning that the spurious changes in diffusion data obtained (e.g. in figure 4 for $P = 0.6, 0.7$) for some particular situation can be rationalized by the conjecture of site blocking. The strong dipole moment of water molecules and their ability to form hydrogen bonds to solid surfaces and neighbouring water molecules generally affect the structural and dynamical properties of water in the presence of ions. Even after a large number of experimental and theoretical investigations of 2D systems the microscopic mechanism is still not fully understood. This complexity arises partly because of the very complex nature of these fundamental liquids, the aqueous electrolytes.

4. Conclusion

Simulation of a highly correlated system like an ion–dipole mixture requires a careful choice of control parameters. The cut-off in real space should be large enough to avoid corner effects. The Ewald sum is superior to the single cell minimum size method, particularly in the calculation of the distribution function. However, the latter may be employed before equilibrium is reached. The present work has given careful consideration to these effects and the results are in fair agreement with different data encompassing the field and analysed in the light of 2D systems.

In this work, a typical 2D system that is in contact with the bulk system and can accommodate a maximum of 100 particles, both ions and dipoles, within a constant area has been simulated. A considerable region of the 2D space is occupied by cavities of different shapes and sizes depending on the various configurations. Each diffusion datum obtained is the average over at least three configurations. In the high temperature range the variation of $\log D$ is simpler than that in the low temperature range. This characteristic feature of the temperature dependence of $\log D$ for various number densities of water molecules for a two-ion system is shown by enlarging the scale in the low temperature region. Each datum can be classified and better understood by comparing it with the Arrhenius form, which points to the restrictions on the motion of the ions in two dimensions compared to that in three dimensions of the same system. So special emphasis may be given on the restrictions to understand the transport in two dimensions.

The concentration dependence of diffusion coefficient in the low temperature region suggests a structural transition (which is a first order phase transition). To make conclusive inferences the system has to be studied very thoroughly in the low temperature region. All these variations show a regularity, with the exception of some spurious changes which are conjectured to be due to site blocking. The temperature dependence of the diffusion coefficient indicates another sharp transition, which was identified as a glass transition; after scaling it with the T/K it can be compared with the experimentally obtained results.

The decrease of this temperature with lattice dilution requires further investigation regarding the short time dynamics and the structure of the interlayer water molecules in aqueous electrolytes. This may be done provided that the size of the system is enhanced. For that elaborate work is to be carried out with a system of larger size and the necessary modifications to incorporate the structure of interlayer water molecules and the short span of existence of

those molecules at a particular site. Dislocations are indeed unimportant at low temperatures and a dislocation-unbinding transition controlled by the terminus of a fixed surface is to be parameterized. This is in agreement with the Kosterlitz and Thoules proposal in which the topological order of solid phase is destroyed by the dissociation of dislocation pairs.

Since both types of ion have the same magnitude of charge density either one is sufficient to represent the trend. However, for each modification the data indicate the existence of a liquid–glass transition and also that state points inside the coexistence region evolve in time and separate into two phases characterized by different densities, structures and mobilities. The slowing down of the particle dynamics in the supercooled state points to excellent opportunities for practical applications.

Acknowledgments

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References

- [1] Onsager L and Samaras N T 1934 *J. Chem. Phys.* **2** 528
- [2] Fujiwara K *et al* 2003 *Langmuir* **19** 2658 and references 1–7 cited therein
- [3] Chakrabarti H 1995 *Phys. Rev. B* **51** 12809
- [4] Carlie C J and Adams M A 1992 *Physica B* **182** 431
Ronne C, Astrand P-O and Keiding S R 1999 *Phys. Rev. Lett.* **82** 2888
Swenson J *et al* 2001 *Physica B* **301** 28
- [5] Lo W Y, Chen K Y and Henderson D 1993 *Mol. Phys.* **80** 1021
- [6] Binder K 1979 *Monte Carlo Methods in Statistical Physics* ed K Binder (Berlin: Springer) p 1
Binder K and Stauffer D 1984 *Applications of the Monte Carlo Methods in Statistical Physics* ed K Binder (Berlin: Springer) p 1
- [7] Ying S C, Veittulainen I, Merikoski J, Hjelt T and Alanissila T 1998 *Phys. Rev. B* **58** 2170
- [8] Chakrabarti H and Pal B 1996 *Indian. J. Phys. A* **70** 729
- [9] Foret I and Wurger A 2004 *Langmuir* **20** 3842
- [10] De Leeuw S W, Perram J W and Smith E R 1980 *Proc. R. Soc. A* **373** 27
- [11] Chakrabarti H and Pal B 2004 *Indian J. Phys.* **78** 935
- [12] Chakrabarti H 1996 *J. Phys.: Condens. Matter* **8** 7019
- [13] Stanley E 1999 *Pramana—J. Phys.* **53** 53
- [14] Kosterlitz J M and Thouless D J 1973 *J. Physique* **6** 1181