DIFFUSION THROUGH CROWDED ENVIRONMENT: AN MD SIMULATION STUDY

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By

Sayantan Acharya
Registration Number: 10CC16J26017

Under the guidance of

Dr. Sarika Maitra Bhattacharyya
(Research Supervisor)

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To those who inspired it and will not read it...

Maa and Baba

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”Two roads diverged in a yellow wood,
And sorry I could not travel both...”

I love making and digging up interesting stories. So, I made films and did my Ph.D side by side and tried my best to enjoy both. In search of true interesting events and the reasonings behind those I managed to finish this thesis. I believe Ph.D is a very demanding process. It demands tenacity and penitence and energy and optimism and skill to an extreme extent in the prime time of one’s life. And It drains one out physically and emotionally some days, and also gives one a kind of self-believe, teaches one to sustain, keeping up the spirit and hope every day. At the end the roller coaster ride reforms one in a complete new way.

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Finally, I conclude my acknowledgement with the words by *Robert Frost* on which I wish I can be loud one day,

“ I shall be telling this with a sigh
Somewhere ages and ages hence:
Two roads diverged in a wood, and I
I took the one less traveled by,
And that has made all the difference.”

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Abstract

"In three words I can sum up everything I've learned about life: it goes on."

- Robert Frost,

According to Fick's law, particles (molecules, atom, ions etc.) tend to move from high concentrated regime to regime where the concentration is low driven by concentration gradient. We call this motion as diffusion. However, there are multiple definition and equatuions exist to explain diffusion, we focus only on the Stokes-Einstein equation. According to this equation the diffusion of tracer particles are found to be inversely proportional to its radius. But in several instances, and scientific experiments, people have seen this law to be violated for a certain range of solute radius. In this thesis we try to understand and unfold some of these unexplained phenomena. Through performing computer simulation studies of few different types of systems and also proposing some new theories we try to achieve our goal.

In the first chapter we introduce the problems we study in this thesis, and talk about the backstories behind each problems. In the second chapter we describe the methods, tools and few definitions we have used in our work.

In the third chapter, we study the diffusion of small solute particles through solvent keeping the solute-solvent interaction repulsive and varying the solvent properties. The study involves computer simulations, development of a new model to describe diffusion of small solutes in a solvent and also mode coupling theory (MCT) calculations. In a viscous solvent a small solute diffuses via coupling to the solvent hydrodynamic modes and also through the transient cages formed by the solvent. The model developed can estimate the independent contributions from these two different channels of diffusion. While the solute diffusion in all the systems show an amplification, the degree of it increases with solvent viscosity. The model correctly predicts that when the solvent viscosity is high the solute primarily diffuses by exploiting the solvent cages. In such a scenario the MCT diffusion performed for a static solvent provides a correct estimation of the cage diffusion.

Next, we present a study of the dynamics of small solute particles in a solvent medium where the solute is much smaller in size, mimicking the diffusion of small particles in crowded environment.

The solute exhibits Fickian diffusion arising from non-Gaussian Van Hove correlation function. Our study shows that there are at least two possible origins of this non-Gaussian behaviour: the decoupling of the solute-solvent dynamics and the intermittency in the solute motion, the latter playing a dominant role. In the former scenario when averaged over time long enough to explore different solvent environments, the dynamics recovers the Gaussian nature. In the case of intermittent dynamics the non-Gaussianity remains even after long averaging and the Gaussian behaviour is obtained at a much longer time. Our study further shows that only for an intermediate attractive solute-solvent interaction the dynamics of the solute is intermittent. The intermittency disappears for weaker or stronger attractions.

In the fifth chapter, we present a comparative study of size dependence of diffusion for charged and neutral solutes in water. Although both show nonmonotonicity of the size dependence of diffusion, their nature and origin are quite different. For neutral solutes, the peak position and the value of diffusion at the maximum are both independent of the solutewater interaction. Interestingly, for charged solutes, with an increase in solutewater interaction strength, the peak position shifts to lower solute sizes and with an increase in charge, it shifts to higher solute sizes. The diffusion value at the peak reduces with an increase in both solutewater interaction and solute charge. We show that all these features observed for charged solutes can be understood in terms of the interplay between ionic and nonionic interactions which is definitely absent for neutral solutes. Some of the earlier studies addressing the nonmonotonicity in diffusion did suggest the interplay between the two interactions to be the cause. However, this is the first time we show that such an interplay gives rise to the nonmonotonicity in the potential energy which is a prerequisite for obtaining the nonmonotonicity in the diffusion. Such nonmonotonicity in the potential energy is absent for neutral solutes.

In the final chapter, we try to summarize the problems addressed and studied in this thesis and discuss about future scopes.

List of Publications

1. **S. Acharya**, M. K. Nandi, A. Mandal, S. Sarkar and S. M. Bhattacharyya, *Diffusion of Small Solute Particles in Viscous Liquids: Cage Diffusion, a Result of Decoupling of SoluteSolvent Dynamics, Leads to Amplification of Solute Diffusion*, J. Phys. Chem. B, **119**, 11169 (2015).
2. **S. Acharya**, U. K. Nandi and S. M. Bhattacharyya, *Fickian Yet Non-Gaussian Behaviour: A Dominant Role of the Intermittent Dynam- ics*, J. Chem. Phys. **143**, 174504 (2017).
3. **S. Acharya**, U. K. Nandi and S. M. Bhattacharyya, *Comparative Study Of Anomalous Size Dependence Of Charged And Neutral Solute Diffusion In Water*, J. Phys. Chem. B 138, **124505** (2019).

CHAPTER 1

Introduction to Diffusion In Crowded Environment

> "I have never started a poem yet whose end I knew. Writing a poem is discovering."
>
> *Robert Frost*

1.1 Diffusion and Stokes-Einstein Relation

Study of transport properties, especially self-diffusion coefficient, D, is a long standing problem in widely different crowded environments, such as proteins in cytoplasm, personal care products through skin membrane, metallurgy, zeolites, clay metals etc. People have been extensively studying the nature of the size dependence and the other factors like solvent viscosity and structure which controls the diffusion of particles in these systems. Different theoretical approaches have been proposed to understand its nature. This report is dedicated to the molecular dynamics investigations in neutral and ionic liquids and the probable origins of the anomaly found in the nature and trend in self-diffusion in solute-solvent systems having a range of solvent viscosity in both ionic and neutral liquids.

Diffusion is often measured by the famous Stokes-Einstein (SE) Relation. For a tagged particle in a liquid of density $\rho(x,t)$, if we consider the diffusion equation,

here D is the diffusion coefficient of the tracer. The mean square displacement (MSD) is a measure of the average squared distance that a particle travels. We define MSD as,

If we take a derivative of Eq.**??**, it gives a relation between MSD and diffusion,

After applying the boundary conditions,

which implies $< x^2 >= 2Dt$.

LHS of Eq.**??** can be calculated directly from the relation,

where v(t) is the velocity of the particle. We take the time derivative of Eq.**??** and we use the invariance of time-translation to obtain,

For a particle of mass m, using the Langevin equation we link the diffusion coefficient to friction,

where ζ is the friction coefficient and $f(t)$ is the fluctuating noise of the system, the time average of $f(t)$ should be zero and to ensure the balance between amplitude of the temperature and noise, the second moment of it should be delta-correlated in time , where k_B is the Boltzman constant and T is the temperature of the system. We solve Eq.**??** to get the instantaneous velocity in terms of the initial velocity $v(0)$ and the noise,

Now, noise and velocity doesn't correlate. So, we can write,

By using Eq.**??**, Eq.**??** and Eq.**??** for $t \to \infty$ limit we get,

Where

At a given temperature T this is the Einstein relation between diffusion coefficient (D) of the Brownian particle and the friction coefficient (ζ) of the liquid. Now, to link with viscosity η in this relation, we use the Stokes formula. This formula relates friction coefficient ζ and viscosity η as,

$$\zeta = C\eta R, \tag{1.1}$$

where C is a constant and R is the radius of the particle. Now, from the last two equations we obtain the "Stokes-Einstein"(SE) relation given by,

The equation predicts an inverse dependence of the solute diffusion, D, on the solvent viscosity, η, and solute radius R.

1.2 Anomalous Diffusion

The study of transport, in simple and complex fluids and also biological systems, has always been an extremely important field of research. Many a times the understanding derived from simple systems helps us understand the more complex ones. Amongst the transport properties, the self-diffusion coefficient is the one, studied extensively both in experimental and theoretical work. Phenomenon such as adsorption, separation, catalytic activity etc, are found to be dependent on self diffusion[**? ? ?**]. Now, we know the self diffusion in simple liquids is usually described by the Stokes-Einstein (SE) relation which was first derived by Einstein to address the diffusion of a "Stokes" particle undergoing Brownian dynamics[**? ? ?**].
where $s = 6$ for stick boundary condition and 4 for slip boundary condition. This powerful equation although derived in the hydrodynamic limit where the solvent appears to be a continuum to the solute, is found to be valid even at microscopic levels where the solute and the solvent are of similar sizes. According to the mode coupling theory (MCT) since both the friction which describes the diffusion and the viscosity are determined by the solvent structures and its dynamics thus the

relation between them is valid even at the microscopic level [?]. According to this study as long as the solute friction is determined primarily by the solvent dynamics the SE relation will hold.

However, even for simple liquids the SE relationship in some cases is found to breakdown [?].

In case of supercooled liquids the breakdown of this relationship is connected to the system developing different dynamic domains and becoming heterogeneous[? ? ? ? ? ? ?]. The diffusion of small solute particle is also known to show a deviation from the SE relation [? ? ? ? ? ? ? ? ?]. Different experimental, theoretical and computational simulation studies attribute this deviation to apparently different phenomena.

Decoupling between solute and the solvent

In some cases an empirical modification of the SE relation, assuming a fractional viscosity dependence, is used to explain the deviation [? ? ? ? ?]. However, the origin of the micro-viscosity/fractional viscosity and the effective radius, are not well understood. Bhattacharyya and Bagchi have shown that the small solutes have faster dynamics than the solvent[?]. This leads to the decoupling between the solute and the solvent. In such a scenario although the solvent viscosity is primarily determined by the solvent structure and its dynamics the solute friction/diffusion due to the decoupling becomes independent of the same. This decoupling leads to the lowering of friction giving rise to larger diffusion[?] which leads to the breakdown of SE relation. In another study it was shown that for smaller solute this deviation becomes stronger at higher density [?].

Levitation Effect in Neutral Solute

Many a times the breakdown marks changes appearing in the system and its transport mechanism. In another study an effective radius, determined by the solute-solvent size ratio is assumed to provide the correct results [?].

Sharma and Yashonath have argued that small solutes explore the solvent cages and when the interaction between the solute and the solvent is attractive, for certain solute sizes there is a force balance which leads to faster diffusion of the solute through the cage[? ? ? ?]. This effect which is known as Levitation effect is responsible for the breakdown of the SE relation[?]. From all these seemingly contradictory results it is difficult to conclude what change in the transport phenomena leads to the breakdown of SE relation for small solutes (Fig. 1.1).

In chapter 3 we study the diffusion of small solute particles over a range of solute diameters. The solvent properties are also varied over a large range to explore solvents with both high and low viscosity. Earlier studies have shown that diffusion in strikingly different medium like diffusion in solid porous Zeolites[**?**] and viscous medium show similar characteristics[**?**]. The levitation effect arising in the porous system, due to the cage diffusion is also present in the latter. This similarity has been explained in terms of presence of transient solvent cages in a solute-solvent system.[**?**] Note that when the dynamics of the solute is faster than the solvent, for a certain time, the latter will appear like a solid to the former. Only in this limit the solute can explore these solvent cages. Thus in a solute-solvent system there exits two different modes of diffusion, the viscous diffusion and the cage diffusion. We develop a model of solute diffusion which describes the diffusion of the solute when it is coupled to the solvent hydrodynamic modes and also can diffuse through the solvent cages. Since the cage diffusion is a phenomena where the solvent appears like a solid to the solute we model this using the concepts of Oscillator model proposed by Bhatia and coworkers to describe the diffusion of a particle through a solid cylindrical nanopore [**? ? ?**]. Oscillator model has successfully described the size dependence of solute diffusion both for attractive and repulsive interactions[**? ?**].

Levitation Effect in Ionic Solute

Anomalous diffusion of ions in water or any other polar solvent is a long-standing problem [**? ? ? ? ? ? ?**]. According to Walden's rule, ionic conductivity, i.e. diffusion of ions should be inversely proportional to the ion radius [**? ? ? ?**]. However, in polar solvents, this relation is not followed. There is a breakdown in the linear behavior, and a size dependent peak in the conductivity is observed. Over the years, several theories developed by different groups have been put forward to explain this anomaly[**? ? ? ? ? ? ? ? ? ? ? ? ? ? ? ?**].

In the continuum picture[**? ? ? ? ? ? ? ? ? ? ? ?**], the friction on the ion has a viscous and a dielectric part. The dielectric friction is higher for smaller sizes whereas the viscous friction for larger sizes. An interplay between the two terms gives rise to a diffusivity maximum (Fig.

1.2). There have also been molecular theories like that of Wolynes[?] where the friction on an ion was separated into that arising from the soft and hard part of the potential. The theory in certain limits reproduced the continuum picture. Later, Bagchi and co-workers[? ?] have extended this approach by including the intermolecular orientational correlations of the solvent as well as the self-motion of the ion. According to their study, the diffusivity maximum arises due to cancellation between hard-sphere and electrostatic part of the interaction. Lee and Rasaiah have done detailed computer simulation studies of the nature of diffusion of alkali and halide ions in water as a function of their size and also the structure and dynamics of the water around these ions [? ?]. The authors could reproduce the experimental results [? ? ?] and show that the structure and dynamics of a solvent cage around an ion vary with the size of the ion. Rasaiah and coworkers have also done a comparative study of different theories and their approximations were tested against simulation results [?]. Chandra and coworkers, through a simulation study, tried to connect this size dependency of the diffusivity maximum with hydrogen bonding [?].

Ghorai and Yashonath[?] have studied the size dependence of the diffusivity in a model system of charged solutes in water. They have shown that above a certain value of the charge, the system shows a diffusivity maximum which they claimed as the Levitation effect (LE) observed in their earlier studies on neutral systems [? ? ? ? ? ?]. The concept of Levitation is usually connected to force balance. According to the authors, for attractive solute-solvent interaction, the small solutes while passing through the transient solvent cages feel an attraction towards one side and thus get stuck which gives rise to reduced diffusion. However, when the size of the solute is about 80% of the size of the opening of the cage, the attractive forces from all directions become equal but opposite,causing a force balance. This allows the solute to freely pass through without getting attached to the wall. The studies suggest that this force balance is universal and is responsible for the diffusity maximum observed in case of charged and neutral solute systems.

Neighbor shell rearrangement

In some recent works, people have related diffusivity maxima of tracer particles in ionic systems with the rearrangement of the solvation shell which can be explained in terms of fluctuation of the ion coordination number[? ? ?]. According to the theoretical model prescribed by Orekhov[?]

motion of a solute particle is correlated with the motion of the solvation shell formed around it and the motion from the rearrangement of the shell (Fig. 1.3). So, the overall diffusion of the solutes can be estimated as a sum of contributions from both viscous part and neighbor shell rearrangement. The author claimed that, for some intermediate solute sizes, the solute-solvent interactions are comparatively low, so, the fluctuation in the coordination number is more and thus its contribution to solute diffusion value is more leading to diffusivity maxima.

In this work, we calculate the co-ordination number (CN) around a single solute particle over the time frames in two different ways. As calculated in [**? ? ?**], the ion coordination number is determined as,

$$N_c = \sum_{i=1}^{N_{neutral}} \frac{1-(d/d_0)^{24}}{1-(d/d_0)^{48}}. \tag{1.2}$$

Here, d_0 is a distance from ion to the first minimum of Radial distribution function (RDF) and d is ion-molecule distance. To avoid the fractional jumps we also calculate the CN just by counting the integer numbers (N_r) in the first neighbor shell. The distance between the solute and the first solvation shell is measured in our calculation as the position of the first minimum of RDF. We consider every changes in the numbers of CN and count a jump every time. Finally, we plot a probability distribution of these jumps to understand the significance of these jumps or rearrangement in solvation shell in solute diffusion value.

1.3 Fickian but Non-Gaussian

There are other aspects of diffusion in solute-solvent medium. Another behaviour which is being observed, is the diffusive particle usually show a Gaussian distribution of probability displacement or van Hove correlation function.

These two events, the diffusive regime and Gaussianity of van Hove function are mutually correlated. Mathematically this can be shown. From continuity equation we know,

The corresponding constitutive equation by Ficks law is,

This assumes the dynamics to be diffusive (Fickian) where, D is self-diffusion constant. Combining these two equation gives the diffusion equation:

in reciprocal space,

Where $\rho_k^{(s)}$ is a Fourier component of the tagged-particle density at t=0. If we multiply both sides of last Eqn by $\rho_{-k}^{(s)}$ and average over initial conditions, we find the normalized correlation function is,

Where n is the total number of tagged particles and we have used the fact that the coordinates of tagged particles are mutually uncorrelated. Now, we know, that the self-part of the density autocorrelation function given in hydrodynamic limit as,

Van Hove self correlation is actually the Fourier transform of this equation,

This is clearly Gaussian in nature. So, mathematical prediction says, for Brownian particles, when the diffusion is Fickian then distribution of probability displacement will be Gaussian in nature.

Although these relations are believed to be valid in only for macroscopic particles even for microscopic particles these behaviours are usually found to be present.

Diffusion of smaller particles in a crowded medium is ubiquitous in nature and has huge industrial and academic relevance [**? ? ? ? ? ? ? ? ? ? ? ? ?**]. The diffusion of sodium chloride through granular soil bed is important in understanding the ground water contamination from solid waste landfills [**?**]. In the study of conductance in polyelectrolytes the knowledge of salt diffusion in polar polymer matrix is important. In metallurgy we need to have the knowledge of diffusion of alloying elements like hydrogenated titanium powder into metal matrices like Titanium [**?**]. The diffusion of protein in cytoplasm, colloidal beads through dense actin filament network, mimicking the cytoskeleton [**? ?**], skin care products through membranes can also be modeled in terms of small particle diffusion in crowded medium. The diffusion of the solute particle depends on its size, its interaction with the solvent and also the dynamics and the structure of the solvent [**?**]. When the mean square displacement is linear with time then the solute is expected to follow the laws of Brownian motion originally derived by Einstein to explain the diffusion of a large solute molecule through a medium [**? ? ?**].

Diffusing diffusivity

According to the theory of classical random walk a system which shows Brownian motion/Fickian diffusion should also have Gaussian distribution of the displacement probability [**?**]. However, there have been a number of studies on a diverse range of systems showing the Fickian but non-Gaussian behaviour [**? ? ? ? ? ?**]. Usually, this phenomena is attributed to the slow changing environment compared to the timescale of motion of the small diffusing particle (solute) [**? ? ? ?**] (Fig. 1.4). It has been argued that this can lead to changing diffusivity of the solute as the solvent environment changes and has been termed as diffusing diffusivity [**? ?**]. The diffusing diffusivity leads to Fickian but non Gaussian behaviour at short times, however the displacement distribution is shown to become Gaussian at longer times [**? ? ? ?**]. Granick[**? ?**] and group has explained the overlap of multiple van Hove plots with different widths arising from different diffusive regime is causing the non-Gaussianity of the resulting van Hove function.

Dynamic heterogenity

Note that, in supercooled liquids, although there is no timescale difference between the solute and the solvent dynamics, and the solute particles are seen to be diffusive, a similar observation of non-Gaussian distribution of displacement probability (van Hove function) has also been observed (Fig. 1.5). In supercooled liquids and granular medium, domains of different dynamical properties (fast and slow) form and the diffusion is found to become intermittent due to the formation of these domains [**?**]. This intermittency of the solute particles is probably the reason for the non Gaussianity in the van Hove function. Chaudhuri $et\ al$ have also shown that the dynamic heterogeneity which leads to the decoupling of the diffusion and the structural dynamics is responsible for the tail in the distribution function.

There has also been studies (single particle tracking microscopy in biological cells) where this anomaly in the dynamics has been attributed to weak ergodicity breaking [**?**]. They have discussed the behaviour of the time averaged mean squared displacement for two prominent stochastic processes. These are fractional Brownian motion and continuous time random walks.

Thus we find that this Fickian but non-Gaussian behaviour of the dynamics is omnipresent in a wide range of systems.

1.4 Thesis outline

chapter 1 In this chapter we introduce the problems we have explored in the whole thesis.

chapter 2 Here, we have explained the tools we have used in our study.

chapter 3 In this study we show that even for repulsive solute-solvent interaction the cage diffusion is responsible for the amplified solute diffusion. However the study further shows that the exploration of the solvent cage is only possible when the solvent viscosity is high and there is a decoupling between the solute and the solvent dynamics. Fitting our model to the simulation results we can estimate the contribution from the viscous diffusion and the diffusion due to cage exploration. Thus the study bridges the gap between studies[**? ?**] presenting apparently contradictory explanations of the origin of the breakdown of the SE relation for small solutes.

chapter 4 Here, we present a comparative study of diffusion of both charged and neutral solutes in water. We show that although both the charged and the neutral solute systems show a diffusivity maximum, their nature and their origin are different. For the charged solute system, the potential energy of the solute as a function of its size shows a nonmonotonicity which arises from the interplay between the ionic and the nonionic parts of the interaction. We also show that this nonmonotonicity is a prerequisite for obtaining the diffusivity maximum for charged solute systems. On the other hand, for neutral solute systems which exhibit such diffusivity maximum, nonmonotonicity in the potential energy is absent.

chapter 5 In chapter 5 we aim to explore the origin of this non-Gaussian behaviour in details via computer simulation studies. We study diffusion of small solute particles through solvent molecules where the solvent molecules are always bigger in size compared to the solute. We vary the mass of the solvent and also the solute-solvent interaction energy from repulsive to strongly attractive. We find that in most of the cases the solute dynamics are Fickian but non-Gaussian. Our study reveals that there are two possible origins of non-Gaussian distribution of displacement probability, one arising from decoupling of the solute from the solvent dynamics and the other from intermittency in the solute motion. For systems which show only decoupling in dynamics, when averaged over a long time the probability distributions recover their Gaussian nature but for systems where the solute dynamics is also intermittent the displacement probability distribution remains non-Gaussian, even at long times. The intermittency seems to provide dominant contribution in the non-Fickian dynamics.

chapter 6 Here, we have discussed about the future scopes and possibilities about the studies we have presented in this thesis.

CHAPTER 2

Definitions, Methods and Models

> "We dance round in a ring and suppose, but
> the secret sits in the middle and knows."
>
> *Robert Frost*

We have discussed about the anomaly found in the diffusion behaviour and the fact that unexpectedly some particles show fickian diffusion although the distribution of displacement or the van Hove function is found non-Gaussian. Here we describe some of the useful and relevant definitions used to compute the different quantities and tools we have used in our study.

2.1 Calculation of dynamical properties

2.1.1 Diffusivity

The diffusion coefficient, D can be obtained from both mean-square displacement (MSD) and velocity autocorrelation function (vacf). We calculate the MSD as,
where, $r_i(t)$ is the position at time t and N is the number of particles. From the long time behaviour of MSD, the diffusion coefficient D can be written as,
At longer time by fitting the MSD with time, we obtain D from the slope of the fitted plot.

The diffusion value can also be obtained from vacf as,
where, $v_i(t)$ is the center-of-mass velocity of a single molecule at time t.

2.1.2 Relaxation time

Relaxation time is the time after when the system forgets its initial conditions or the correlation goes away.

The relaxation time (τ) is the characteristic time that a system takes to go spontaneously (owing to incessant atomic motions) from a given microscopic configuration at an arbitrary initial time t = 0 to another completely uncorrelated microscopic configuration.

The relaxation time can also be explained as the time taken by a system to go back to the equilibrium after it was sud- denly taken out of equilibrium condition at t = 0. Generally, it is measured from the decay of appropriate correlation functions.

2.1.3 Overlap function

The dynamics is also studied is this thesis by a two-point time correlation function of local density, which is called the overlap function (q(t)), and it is defined below as,

Here we have implied the averaging over time origins t_0. Like $F(\vec{k},t)$, overlap function can also be separated into self and distinct terms:

In this work, the self part is calculated by neglecting $j \neq i$ terms in the double summation. Here, we examine the self part of the total overlap function based on the observations that the results obtained from the self part are not signicantly different from the observations are obtained by considering the collective overlap function.

Further, for numerical computation, a window function w(x) is used to approximate the δ function. The condition of overlap between two particle positions separated by a time interval t can be defined by the window function as,

However, this time dependent overlap function depends on the choice of the cut-off parameter a, which we take as 0.3. The choice of this parameter is such that particle positions separated by the small amplitude vibrational motion are treated as the same, or that a^2 is comparable to the value of the MSD in the plateau between the ballistic and diffusive regimes.

2.2 Calculation of static properties

2.2.1 Radial distribution function

The particle distribution functions intends to measure how much structure of a fluid can deviate from complete randomness. Radial distribution function (rdf) defines the probability of finding a particle from another tagged particle at a distance r. The RDF is primarily dependent on the attraction of the particles so will vary greatly for solids, gases and liquids.

If the radial distribution function g(r) of the system is known the thermodynamic properties can be obtained via various ways.

This radial distribution function or pair correlation function, $g(r)$, is nothing but the probability of finding a particle at a distance r from a tagged particle and thus, it describes how the density varies as a function of distance from a reference particle. In Fig.**??** a typical radial distribution function is shown for spherical particles in a homogeneous system.

The definition of radial distribution function g(r) is given by writing the probability of a configuration of N particles in equilibrium with a heat bath at temperature T in a volume V :

Here and are potential energy.

We write the probability of the particle 1 is in the volume $d\mathbf{r}_1$ around r_1 and particle 2 is in $d\mathbf{r}_2$ around r_2 from Eq. (**??**) as,

We define the pair distribution function as,

here ρ is the homogeneous density of the system.

For N particle system the local particle density can be defined as and the density function of a single particle is

This ensemble average is not dependent on particle label. For one particle we compute the average. The average can be written as,

Similarly, for two particle systems, the density distribution function is,

Using the same logic for single particle density function, the prev Eq.(**??**) can be written as,

From last equation we can write $g(\mathbf{r}_1, \mathbf{r}_2)$ as,

Now if we express the right hand side of Eq.(**??**) as,

Hence, for isotropic and homogeneous system we can write,

For a binary system the pair correlation function is given by,

Here system volume is V, N_α is the number of particle of type α and the position of $i-$th particle is r_i.

2.2.2 Static structure factor

The static structure factor $S(\mathbf{k})$ is a mathematical description of how incident radiation is scattered by a material and the correlations between the positions of the particles in the fluid is calculated by us as,

where, $\rho_\mathbf{k}$ is a Fourier component of $\rho(r)$ (local particle density). It can be defined as $\rho(r) = \sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{r_i})$, where N is the number of particles in the fluid and it is given by,

and **k** is the wave vector. So, $S(\mathbf{k})$ can be written as, Now, we relate the Fourier transform of g(r) with the static structure factor $S(\mathbf{k})$. First, we devide the above mentioned sum into self, i=j, and distinct, $i \neq j$, contributions. Then Eq. (**??**) looks like,

We can write from Eq. **??**, using the definition of $g(\mathbf{r}_1, \mathbf{r}_2)$,

Homogeneous and isotropic fluid, $g(\mathbf{r}_1, \mathbf{r}_2)$ only depends on $|\mathbf{r}_1 - \mathbf{r}_2|$:

The partial structure factors $S_{\alpha\beta}(\mathbf{k})$, for binary mixture, can be defined as,

For MCT calculation the partial structure factor data can be used.

2.2.3 Pair excess entropy

By using Kirkwood factorization [**?**] of the N-particle distribution function [**? ? ?**], the excess entropy S_{ex} can be expanded in an infinite series,

S_n are partial entropies which can be obtained by a suitable re-summation of spatial density correlations involving n-particle multiplets. The pair excess entropy S_2 for binary system reads as,

where density of the system is ρ, $g_{\alpha\beta}(r)$ is the atom-atom pair correlation function between type α and type β, x_α is the mole fraction of type α and the Blotzmann constant is k_B. The residual multiparticle entropy (RMPE) is $\Delta S = S_{ex} - S_2$. It contains the higher order (beyond two body) contribution to the excess entropy [**? ? ? ?**].

2.3 The model and simulation details

We have performed an extensive molecular dynamics simulations for three-dimensional monodisperse as well as binary mixtures in the canonical ensemble. The system contains total N number of particles with density $\rho = N/V$, where V is the volume of the system. The system is under periodic boundary conditions. For binary mixtures total N contains N_A particles of type A and N_B particles of type B. The models studied here, are the well-known models of glass-forming liquids: the binary Kob-Andersen Lennard-Jones (LJ) liquids [**?**] and the corresponding WCA version (WCA) [**?**], the binary network forming (NTW) model [**?**] and one-component Gaussian core model (GCM) [**?**]. The molecular dynamics (MD) simulations have been carried out using the LAMMPS package [**?**]. For all state points, three to five independent samples with run lengths $>$

100τ (τ is the α- relaxation time) are analyzed.

We have performed MD simulations in the canonical ensemble (NVT) using Nosé-Hoover thermostat with a particular integration timestep depending on the systems.The time constants for Nosé-Hoover thermostat are taken to be 100 timesteps. The sample is kept in a cubic box with periodic boundary condition.

CHAPTER 3

Diffusion of Small Solute Particles in Viscous Liquids: Cage Diffusion, a Result of Decoupling of Solute-Solvent Dynamics,Leads to Amplification of Solute Diffusion

> ”The strongest and most effective force in guaranteeing the long-term maintenance of power is not violence in all the forms deployed by the dominant to control the dominated, but consent in all the forms in which the dominated acquiesce in their own domination.”
>
> *Robert Frost*

3.1 Introduction

We study the diffusion of small solute particles through solvent keeping the solute-solvent interaction repulsive and varying the solvent properties. The study involves computer simulations, development of a new model to describe diffusion of small solutes in a solvent and also mode coupling theory (MCT) calculations. In a viscous solvent a small solute diffuses via coupling to the solvent hydrodynamic modes and also through the transient cages formed by the solvent. The model developed can estimate the independent contributions from these two different channels of diffusion. While the solute diffusion in all the systems show an amplification, the degree of it increases with solvent viscosity. The model correctly predicts that when the solvent viscosity is high the solute primarily diffuses by exploiting the solvent cages. In such a scenario the MCT diffusion performed for a static solvent provides a correct estimation of the cage diffusion.

The next section contains Simulation Details. Section 3 contains the Results and Discussion followed by Conclusion in section 4.

3.2 Simulation Details

In this work we perform an equilibrium Molecular Dynamics simulation with an atomistic model where particle type 'i' is interacting with particle type 'j'with truncated and shifted Lennard-Jones (LJ) pair potentials, given by

Where $\Phi_{ij}{}^{LJ}(r_{ij}, \sigma_{ij}, \epsilon_{ij}) = 4\epsilon_{ij}[(\frac{\sigma_{ij}}{r_{ij}})^{12} - (\frac{\sigma_{ij}}{r_{ij}})^{6}]$, r_{ij} is the distance between pairs, $r_{ij}{}^{c} = 2^{\frac{1}{6}}\sigma_{ij}$ for Weeks-Chandler-Andersen (WCA) system [**?**] and $r_{ij}{}^{c} = 2.5\sigma_{ij}$ for LJ system. Here $i, j = 1, 2$, where 1 refers to solvent and 2 refers to solute. For all the systems we consider that the interaction between the solvent and the solute has a soft core which allows inter-penetration between solute-solvent pair (see Table 1).

We take a system with 1000 particles where 10 of them are solute and rest are solvent. We study four different systems varying the interaction potential, solvent mass and the interspecies interaction length given in the Table 1.

NPT simulations are carried in a cubic box at a reduced temperature T*=1.663, and reduced pressure 7. To avoid crystallization, system 2 is simulated at T*=2. Simulations are performed with time step of 0.001τ, where $\tau = \sqrt{\frac{m\sigma_{11}^2}{\varepsilon}}$. In this study, length and temperature are given in the units of , σ_{11} and $\frac{k_B T}{\varepsilon}$. All the above mentioned systems are equilibrated for 1-2ns followed by a production run of 4ns. Systems with larger mass are simulated with longer equilibration time. The molecular dynamics simulations are carried out using LAMMPS package [**?**].

3.3 Results and Discussion

We find that the solutes in all the systems studied here show an amplification of diffusion. However since the solvent viscosity shows a large variation, in order to do a comparative study of the degree of amplification in different systems, we use the SE relation as a measure. The solvent diffusion at high temperatures is known to be coupled to the viscosity[**?** **?**]. Thus in eq **??** by replacing the η value by the solvent diffusion we can write,
where D_2 is the solute diffusion, D_1 is solvent diffusion, σ_{11} and σ_{22} are the solvent and solute diameters respectively. In **??** we plot $\frac{D_2}{D_1}$ as a function of $\frac{1}{\sigma_{22}}$ (as $\sigma_{11} = 1$).

We find that the deviation from the SE prediction increases with the solvent viscosity. The origin of this is not fully understood. As mentioned earlier, different studies have attributed this large diffusion to apparently different phenomena. In one case it is the decoupling of solute-solvent motion[**?**] and in other case it is the Levitation effect which was found to be responsible for it[**?**]. The later is known to arise from solute exploring solvent cages. As mentioned in the Introduction when the solute dynamics is orders of magnitude faster than the solvent in the initial time the solvent appears like a solid to the solute. This allows the solute to explore the solvent cages. However when the decoupling in dynamics is not strong in later times the solute might also be able to explore the viscous properties of the solvent. Thus a small solute diffusing in a viscous system has two different contribution to its diffusion. In simulation studies of solute diffusion it is not possible to individually make an estimation of these two independent components. In order to decouple these two contributions to solute diffusion we propose a model where the contribution from the solvent hydrodynamic modes is assumed to be given by the SE relation as we assume in this regime the solute the solvent dynamics are coupled and the cage diffusion is modeled using Oscillator Model (OM) [**?** **?**] which was developed for studying diffusion through a nanoporous solid.

3.3.1 Oscillator Model

According to the Oscillator model of Bhatia and coworkers [**? ? ?**], particle diffusing through a cylindrical nanopore at low particle density oscillates along the plane perpendicular to the tube axis. Here, the transport diffusivity of the particle of mass 'm' at temperature T is given by, $D_t = \frac{k_B T}{m} < \tau >$, where $< \tau >$ is the average oscillation time of the trajectory in the nanopore at temperature, T. The bigger the pore, the longer will be the time of oscillation and the collision frequency will reduce. This in turn will reduce the rate of axial momentum loss of the confined particle thus leading to higher diffusion along the pore axis. Following the same logic a similar effect of increase of diffusion value can be obtained by keeping the pore radius fixed and reducing the particle size. Using Hamiltonian equation of motion the oscillation time for a particle moving in a radial potential function can be written as, [**?**]

Where r_{c0} is the radial position at the point closest to center, the point of reflection near the wall is r_{c1} and the radial momentum profile, $p_r(r', r, p_r, p_\theta)$, can be written as,
when $\Phi_{fs}(r)$ is the radial potential field. We get r_{c0} and r_{c1} value by solving $p_r(r', r, p_r, p_\theta) = 0$.

Averaging the oscillation time τ over the canonical distribution of r, p_r and p_θ, the low-density transport coefficient in the presence of a one-dimensional potential field in a cylindrical pore is given by,

where p_r and p_θ are momentum parameters and $Q = \int_0^\infty r e^{\beta \Phi_{fs}(r)} dr$.

It was shown that for hard spheres (HS) systems eq **??** reduces to the classical Knudsen model [**? ?**],

where r_{ph} is the maximum displacement possible from the center of the pore to the pore wall. We calculate the diffusion coefficients D^{WCA} and D^{HS} as obtained from the OM where the interaction between the particle and the nanopore is given by WCA and hard sphere(HS) potentials, respectively. The calculations were done for a fixed size of the nanopore, r_{pore} and varying the size of the diffusing particle, σ_{22}. We compare D^{WCA} and D^{HS} at temperature 1.663 with the classical Knudsen model (**??**). Although all three models predict the diffusive to be linear with r_{ph}, ($r_{ph} = r_{pore} - \frac{\sigma_{22}}{2}$), $D^{Knudsen}$ shows slightly stronger r_{ph} dependence whereas the r_{ph} dependence of D^{WCA} and D^{HS} are similar in nature. The diffusion values for the WCA systems are a bit lower because the length-scale of the WCA potential is larger than the hard sphere (HS) potential making the pore narrower (**??**).

3.3.2 Our Model

As discussed before, in a solute-solvent system the solvents form transient cages through which a small solute can diffuse [**? ?**]. The neck of the cage can be considered as an nanopore. The diffusion of a particle through a neck is similar to that along the pore axis. Thus the Oscillator Model can be used to understand the diffusion of a solute through the transient solvent cages. However unlike a fixed radius of a nanopore the solvent cages have a distribution of neck sizes[**?**]. The distribution can be approximated by a Gaussian function, $g(r_{neck}) = \frac{1}{h\sqrt{2\pi}} \exp -\frac{1}{2}(\frac{r_{neck}-\nu}{h})^2$, where g_{neck} is the distribution of neck size in the solution. r_{neck} is the radius of the neck formed by the solvent particles. ν is the mean position and h is the full width at half maxima of the distribution. From earlier studies we find that $\nu = 0.2\sigma_{11}$ and $h = 0.0583\sigma_{11}$[**?**]. For a repulsive solute-solvent interaction (given by WCA potential) the diffusion of solute through the solvent cages, incorporating the neck size distribution of these cages can be written as,
The second equality is written assuming linear dependence of D^{WCA} on r_{ph} and obtaining the slope 'c' from **??**. The r_{ph} is defined as a function of r_{neck}, which can be written as, $r_{ph} = r_{neck} + r_{pene} - \frac{\sigma_{22}}{2}$. Note that in our model σ_{12} is smaller than that predicted by additive Lorentz-Berthelot rule[**?**] (see Table 1), thus the solute can partially penetrate a solvent particle. The inter-penetration distance is given by $r_{pene} = \frac{\sigma_{11}+\sigma_{22}}{2} - (0.171 + \sigma_{22})$. As shown in the inset of **??** presence of the distribution of neck sizes although predicts a small deviation of the D^{WCA}_{neck} from that predicted by the OM the behavior remains similar.

We describe the diffusion of a solute as a sum of that predicted by the SE relation and the diffusion through transient solvent cages. Note that in the rest of the article the neck diffusion and diffusion through the cage will be used synonymously. The total diffusion can be written as,
P is the average neck population that a solute particle encounters in the timescale of its Stokes-Einstein diffusion. Replacing the expression of D^{WCA}_{neck} (given in eq **??**) in eq **??** the D_{tot} can be written as,
Considering the solvent to follow SE relation eq **??** can be rewritten as,
In the above equation the neck population explored by the solute, P, has been kept as a fitting

Table 3.1: The parameters used in the model systems, where σ_{11}, σ_{12} and σ_{22} are solvent, solute-solvent and solute diameters, respectively, ϵ_{11}, ϵ_{12} and ϵ_{22} are interaction parameters for solvent-solvent, solute-solvent and solute-solute pairs respectively which are scaled by ϵ. Here for all the systems $\sigma_{11} = 1, \epsilon_{22} = 0.5$ and we have considered a range of solute radius as, $\sigma_{22} = 0.073, 0.098, 0.122, 0.171, 0.2, 0.22, 0.244, 0.293, 0.317, 0.366$. Mixed potential is referred to attractive interaction (LJ) between solvent-solvent and repulsive interaction (WCA) between solute-solvent and solute-solute pairs. m_1 is the solvent mass and m_2 is the solute mass which is 1

sys-Potentials	$\frac{\varepsilon_{11}}{\varepsilon}$	$\frac{\varepsilon_{12}}{\varepsilon}$	m_1	σ_{12}
1-WCA	1	1	1	$\sigma_{22} + 0.171$
2-Mixed	3	1	1	$\sigma_{22} + 0.171$
3-Mixed	1	1	10	$\sigma_{22} + 0.171$
4-Mixed	1	1	100	$\sigma_{22} + 0.171$

Table 3.2: Solvent Diffusion values for all the systems. We also present a representative solute diffusion value (for $\sigma_{22} = 0.073$) to show the decoupling of solute-solvent dynamics.

system	D_1	D_2
1	0.182	6.2
2	0.023	5.4
3	0.0273	5.3
4	0.007	5

parameter. Fitting this equation to the simulation results as a function of solute size should give us an estimation of P. Note that systems 2, 3 and 4 show a strong amplification of solute diffusion, thus the diffusion in these systems cannot be explained completely via SE relation (D_{SE}) and should be primarily given by diffusion due to neck exploration, D_{neck}. However D_{neck} shows a linear σ_{22} dependence (inset, **??**) whereas D_{tot} is a nonlinear function of σ_{22} (**??**). Thus the model predicts that in order to fit eq **??** to the simulation data, P should have a dependence on the solute size. We note that a smaller solute which can diffuse faster should explore larger number of cages compared to a bigger solute, thus as predicted by our model, the explored neck population should indeed be dependent on the size of the solute. To incorporate this dependence we consider the population to be a function of D_{SE} and D_{neck}^{WCA}. Thus we write it as,
where α is the proportionality constant.

Replacing eq **??** in eq **??** and using α as a fitting parameter we compare the simulation results with the diffusion values as predicted by our model. We find that our model provides a good description of the σ_{22} dependence of the diffusion for all the systems studied here (**??**). Next we analyze the contributions from the different components of diffusion, D_{SE} and D_{neck} for the different systems as predicted by the model. For system 1 which is less viscous (see Table 2) the larger solute particles diffuse via coupling to solvent dynamics and thus follow SE behavior and the diffusion is given primarily via D_{SE}. However for smaller solutes both the modes of diffusion are active with the neck contributing little more as the solute size is decreased (Fig. **??**). Note that this system shows a weak deviation from SE behavior (**??**). For system 2, 3 and 4 where the solvent viscosity is quite high (see Table 2), the model predicts that the diffusion, specially for smaller solute particles take place primarily via D_{neck} (Fig. **??**,**??**,**??**), D_{SE} has a negligible contribution. The viscosity here has two-fold effects. A system with high viscosity has slower moving solvent thus reducing the motion of the solute which is coupled to it. However, high solvent viscosity and a diffusing solute implies a decoupling between solute-solvent dynamics where the solvent appears like a solid to the solute with long lived transient cages. In this limit the solute diffusion mimics the diffusion through a porous medium and depends only on the static structure of the solvent. This is precisely what we observe when we compare diffusion values of systems 1, 3, and 4 (see **??**) where the diffusion values for system 3 and 4 are almost independent of the solvent dynamics. Note that the dynamics of the solvent in system 3 when compared to system 4 is faster by about a factor of four, whereas the solute dynamics remains same (see Table 2). The observation that diffusion values grow with the growth of the neck diffusion is similar to that reported by Sharma and Yashonath although for an attractive solute-solvent interaction [**?**].

3.3.3 Mode Coupling Theory Prediction

As mentioned earlier according to the study based on MCT calculation it was shown that the decoupling between solute-solvent motion leads to breakdown of Stokes-Einstein prediction [**?**]. Our present study also reveals that this decoupling is essential for exploration of solvent cages which eventually leads to the breakdown of SE relation. In an earlier work involving some of us we have shown that MCT calculations can explain the Levitation dynamics of small solute, even describing the non-monotonic solute size dependence of diffusion for an attractive solute-solvent interaction [**?**]. Given the success of MCT in earlier studies it is impetus to do a MCT calculations for our present systems.

According to MCT the diffusion coefficient of a tagged solute particle can be written as[**?**],

Here $\Gamma(z)$ is the frequency dependent friction. Due to difference in timescale the friction term is divided into two parts , the short time part arises from the binary friction ($\Gamma_B(z)$) and the long time part ($\Gamma_R(z)$) comes from the repetitive collisions which are correlated[**?**],
It has been earlier shown that for solutes having same size or smaller than the solvent the longtime part is dominated by the density contribution[**?**]. However mode-coupling calculations have further predicted that the decoupling of the solute motion from the solvent dynamics leads to the breakdown of the SE relation[**?**]. When there is a complete decoupling between the solute-solvent dynamics the only contribution to the solute friction primarily comes from binary component. Amongst the systems that we have studied here we find that diffusion in the systems with higher viscosity (system 2, 3 and 4) takes place primarily through neck diffusion (**??**). Thus for these systems we can consider a complete decoupling between the solute-solvent dynamics . The diffusion value for these systems as predicted by MCT can be written as,
where, , where ω_{012}^2 is Einstein frequency of the solute in presence of the solvent. It is expressed as,

here $g_{12}(\mathbf{r})$ is the radial distribution function and $\Phi_{12}(\mathbf{r})$ is the inter atomic potential of the solute-solvent pair[**?**]. In the expression of $\Gamma_B(t)$, the relaxation timescale, τ_ς, is determined from the second derivative of $\Gamma_B(t=0)$[**?**],

here $S(q)$ is the static structure factor of the solvent, μ is the reduced mass of the solute- solvent pair. $\gamma_d^{\alpha\beta}(\mathbf{q})$ is combination of the second moments of transverse and longitudinal current correlation function, $\gamma_d^t(\mathbf{q})$ and $\gamma_d^l(\mathbf{q})$, respectively and it is given by, Here, and [**?**].

The MCT prediction for system 2, 3 and 4 are plotted in **??** along with the simulation results. Note that in this calculation the solvent is considered to be static and only its static structural information is required for the calculation of the friction. Our calculation shows that the binary diffusion although slightly overestimates, can explain both the simulation results and the predicted neck diffusion. The marginal overestimation is due to the absence of the density term which has a small contribution to friction. Thus we show that a decoupling between solute and solvent dynamics is essential for the solute to explore the solvent cages and in that case the binary component of the MCT diffusion value can predict the contribution coming from neck diffusion. The success of MCT also implies that in its present framework it can also describe the diffusion through porous medium.

3.4 Conclusions

In this article we present our study of diffusion of small solutes in solvents by varying the size of the solute and also by varying the solvent parameters. The difference between a diffusion of a small and a large solute is that small solutes are known to not only diffuse by being coupled to the hydrodynamic modes of the solvent, which involves density fluctuation and also the transverse and longitudinal currents in the solvent, they can also diffuse through the transient solvent cages if the neck of the cage is big enough to allow the solute through it. The diffusion values as obtained from the simulation studies although contain both the components, are unable to differentiate between them. The present study involves both analytical and computational studies. Computer simulations are performed to obtain the diffusion values and a model is developed to independently access the contribution to diffusion from the solvent hydrodynamic modes and that which is coming from the exploration of transient solvent cages. The exploration of transient solvent cages is similar to the diffusion through a porous solid medium. Thus cage diffusion is modeled based on the OM [**? ? ?**] originally developed to calculate the diffusion of particles through solid cylindrical nanopores.

In our model using a single fitting parameter, which is proportional to the population of the cage explored by the solutes, we can describe the solute size dependence of four different systems in different viscosity regimes. The model correctly predicts that the solutes which diffuse faster is able to explore larger population of the cages. The model can further predict the different diffusion contributions. We find that the contribution from the two different modes (viscous and cage exploration) depends on the viscosity/dynamics of the solvent as compared to that of the solute and the solute-solvent size ratio. For larger solutes the diffusion is primarily given by D_{SE}. However as the size of the solutes are decreased the D_{SE} reduces and D_{neck} grows. When the viscosity of the solvent is large the solute particles show an amplified diffusion and primarily diffuses through the cage mode. In this regime the solute diffusion becomes independent of the properties of the solvent dynamics and it mimics the diffusion through a porous medium where the pores are described by the solvent static structure. In these systems we also perform MCT calculation. We show that the binary collisions which depend only on the static structure of the solvent primarily determines the diffusion. Thus similar to the neck diffusion the MCT calculation is performed for a solvent which is static. The results suggest that the present MCT framework with static solvent is capable of explaining diffusion of solute in a porous medium.

Finally we would like to conclude that the previous observations attributing the break down of the SE relation to apparently two different phenomena, the decoupling of solute-solvent motion [**?**] and the Levitation effect [**?**] are not contradictory to each other. In this present study we deal with systems where the solute-solvent interactions are always repulsive thus there is no force balance and hence no Levitation effect. However the Levitation effect reported earlier and our present study both rely on the ability of the solute to explore solvent cage. As shown in the present study this is possible when there is a decoupling of the solute-solvent dynamics. Thus for Levitation to help the solute diffuse faster the solute dynamics must decouple from the solvent motion so that the solvent cages appear stationary in the timescale of solute dynamics.

CHAPTER 4

Comparative Study Of Anomalous Size Dependence Of Charged And Neutral Solute Diffusion In Water

> "Forgive me my nonsense as I also forgive the nonsense of those who think they talk sense."
>
> *Robert Frost*

4.1 Introduction

In this chapter, we present a comparative study of diffusion of both charged and neutral solutes in water. We show that although both the charged and the neutral solute systems show a diffusivity maximum, their nature and their origin are different. For the charged solute system, the potential energy of the solute as a function of its size shows a nonmonotonicity which arises from the interplay between the ionic and the nonionic parts of the interaction. We also show that this nonmonotonicity is a prerequisite for obtaining the diffusivity maximum for charged solute systems. On the other hand, for neutral solute systems which exhibit such diffusivity maximum, nonmonotonicity in the potential energy is absent.

The next section contains computational details. Section 3 talks about methodology, section 4 includes the results and discussion followed by the conclusion in section 5.

4.2 Computational Details

4.2.1 Intermolecular Potential Functions

Water-Water. We consider the SPC/E water model [**? ?**] in our simulations. This is a three point water structure. The three sites are representing one Oxygen (O) and two Hydrogen (H) atoms. The O-H bond length is 1 Å. The HOH angle is 109.47°. The charge of an individual O atom, q_O=-0.8476e and H atom, q_H=+0.4238e. A short range Lennard-Jones (LJ) potential along with a long range Coulomb potential makes the whole equation look like,

here, ϵ_{OO} and σ_{OO} are LJ parameters between Oxygens of two water molecules and are defined in this model as 0.650 kJ/mol and 3.166 Å respectively. r_{OO} is the distance between them. The charge at site i is q_i.

Solute-Solute. The interaction between two solute particles is considered as a sum of short range LJ and long range Coulomb potential. This is expressed as,

here, the σ_{ss}=1.5 Å and ϵ_{ss}=0.2608 kJ/mol are fixed. We consider the charge on the solute as, $q_s = 0, \pm 0.001e, \pm 0.01e, \pm 0.05e$, $\pm 0.3e$ and $\pm 1.0e$.

Solute-Water. We consider the solutes to be charged spheres. It has a short range LJ interaction with water Oxygen and long range Coulombic interaction with both Oxygen and Hydrogen atoms of a water molecule. The form of the potential looks like,

Here, Φ_{sw}^{LJ} depicts the LJ part of the interaction and Φ_{sw}^{Coul} depicts the Coulombic part of the interaction. σ_{sO} is the solute-Oxygen diameter, r_{sO} is solute-Oxygen distance and r_{sH} is solute-Hydrogen distance. The solute-Oxygen interaction strength is ϵ_{sO}. We have done the study by changing both the ϵ_{sO} and q_s values. In one case we fix and vary interaction as ϵ_{sO}=1.58 kJ/mol, 3.00 kJ/mol and 6.00 kJ/mol. In another case, we keep ϵ_{sO}=1.58 kJ/mol, and vary the charge q_s=0.05e, 0.3e and 1.0e. We allow interpenetration between solute and water, so the σ_{sO} does not obey the Lorentz-Berthelot combination rule. We keep the σ_{ss} fixed but vary σ_{sO} by varying the interpenetration. We take a range of σ_{sO} values as, from 0.9 Å to 1.3 Å with a gap of 0.1 Å, from

1.3 Å to 2.5 Å with a gap of 0.2 Å and 3.0 Å to 5.5 Å with a gap of 0.5 Å. While choosing the range of radius, we make sure that at a small distance, the repulsive part of the LJ interaction between the solute and Oxygen atom of water dominates over the Coulombic interaction. This is especially important in case of -ve charges as for small sizes, the Coulombic interaction between the -ve charge and the Hydrogen atom of water can be very strong and this will result in the -ve charge sitting on the H atom. So, for q=-0.01e and -0.05e, the minimum σ_{sO} value is 1.3 Å, while for q=-0.3e the minimum σ_{sO} value is 1.7 Å. However, note that, for +ve charges, the repulsive part of the LJ potential dominates at small distances and this issue doesn't arise. But since, the simulations are done with an equal number of +ve and -ve charges, we keep the range same for both the charges.

4.2.2 Simulations Details

We perform Molecular Dynamics (MD) simulations using GROMACS package [**?** **?**]. We take 22 pairs of ions and as mentioned above SPC/E model of water. Earlier work by Lee and Rasaiah has shown that simulation studies with SPC/E water model can closely reproduce the experimental results of the size dependence of ionic diffusion[**?**]. Thus our choice of water model is justified. Dilution effect is checked for all charges and the systems with the least number of water molecules which reproduces the results in the dilute regime are used for the analysis. For the system with charge q_s=±1.0e since the ion-ion interaction strength is higher we have 2136 water molecules (4098 water molecules for charge q=1.0e), for the rest of the systems (charges q_s=±0e, 0.01e, 0.001e, 0.05e and 0.3e), we have 851 water molecules.

We use the isothermal-isobaric ensemble (NPT) simulation for equilibration run at T=300 K and a reduced pressure of 0.7 Bar. The production run is done in microcanonical (NVE) ensemble.

The MD simulations are performed in a cubic box using Nosé-Hoover thermostat[**?**] and Berendsen barostat. The integration step is varied for different charges depending on the strength of the ion-water interaction. We have a range of integration steps from 0.6 fs to 0.0002 fs. For smaller sizes and higher charges, integration steps are smaller. Because of the strong interaction, small displacement can lead to a large change in energy. In this study, length and temperature are given in real units. All the above mentioned systems are equilibrated for 150-300 ps followed by a production run of 800-2000 ps. Systems with higher charges are equilibrated over longer times.

4.2.3 Methodology

4.2.4 Calculation of Diffusion Coefficient

The diffusion coefficient, D can be obtained from both mean-square displacement (MSD) and velocity autocorrelation function (vacf). We calculate the MSD as,

where, $r_i(t)$ is the position at time t and N is the number of particles. From the long time behavior of MSD, the diffusion coefficient D can be written as,
At longer time by fitting the MSD with time, we obtain D from the slope of the fitted plot.

The diffusion value can also be obtained from vacf as,
where, $v_i(t)$ is the center-of-mass velocity of a single molecule at time t.

4.3 Results and Discussion

In this work, we study the nonmonotonicity of diffusion as a function of solute size. Although the primary focus of this work is to study the diffusion of charged solutes (ions) in water, for the sake of comparison, we first present a study of the diffusion of neutral solutes in water.

4.3.1 Neutral Solutes

Yashonath and coworkers in their study of diffusion of neutral solutes in water, interacting only via LJ interaction, at T=180K, have shown that for solute-water interaction $\epsilon_{sO} = 1.5846$ kJ/mol there is a nonmonotonicity in the size dependence of diffusion [**?**]. In the present study, we focus on room temperature water dynamics, i.e. T=300K. At room temperature, with solute-water interaction 1.5 kJ/mol the nonmonotonicity in size dependence of diffusion disappears [**? ?**]. Thus, to obtain a nonmonotonicity in solute diffusion, we arbitrarily increase the ϵ_{sO} value to 15 and 22.5 kJ/mol, which is about 10 and 15 times the value used in the earlier study [**?**].

As shown in Fig. **??**a, the diffusion as a function of 1/σ_{sO} does show a non monotonic behavior with a peak at σ_{sO} $\simeq$1.05 Å. Note that, the position of the peak is similar to that obtained earlier[**? ? ?**] but at lower temperatures. Apart from just the presence of diffusivity maximum, there are other observations made from this study. Firstly, the position of the peak doesn't change with the

ϵ_{sO} value. The second observation is that the enhancement of diffusion increases with ϵ_{sO}. We are not going to analyze these results in details as they have already been done in earlier studies [**?**]. Similar nonmonotonic size dependence of diffusion observed in the solute-solvent system has been explained using mode coupling theory where it was shown that a size dependent decoupling between the solute-solvent dynamics and strong solute-solvent attraction leads to the nonmonotonic enhancement of diffusion [**? ?**]. In Fig. **??**b we show that although the diffusion is nonmonotonic the potential energy shows no such nonmonotonicity. We also analyze the probability distribution of first shell water orientation $P(\theta)$, around solute particles where θ is the angle between the vector bisecting the water molecule w.r.t the vector connecting the water Oxygen to the solute (Fig. 4.9a in the Appendix I). We plot the $P(\theta)$ for two different solutes, the biggest and the smallest size studied here which are larger and smaller than the size where the diffusion peak is obtained. We find that water orientation is independent of the size of the solute and is dominated by the water-water hydrogen bonding. We also plot the N_c trajectory around these two solute particles (Fig. 4.9b in the Appendix I). We find that although the value of N_c changes with the size of the solute, the dynamics remain the same. In the rest of the article, we will compare the features obtained for neutral solutes with that of charged solutes and try to understand the diffusion phenomena of charged solutes.

4.3.2 Charged Solutes

Next, we study the diffusion of charged solute particles in water. In earlier studies, it has been observed that for alkali ions there is a nonmonotonicity in the size dependence of the diffusion coefficient[**? ? ? ? ? ?**]. However, for a systematic study of the effect of solute-water interaction and solute charge on the size dependent diffusivity maximum, we start with a neutral solute and slowly increase the charge on the solute. We also fix a value of the charge on the solute and vary the solute-water nonionic interaction strength (LJ part). These model systems, although artificial, provide us a wider range of systems where the nature of the diffusivity maximum changes with solute-water interaction strength and with the charge on the solute, allowing us to explore the effect of the interplay between nonionic and ionic interactions.

Here we first choose $\epsilon_{sO} = 1.5$ kJ/mol. When the solute is neutral, this system does not show any nonmonotonicity at T=300K. Thus, we make sure that this chosen strength of the LJ interaction alone is not enough to produce a diffusivity maximum. In Fig. **??**a and Fig. **??**b we plot the diffusion values as a function of inverse σ_{sO} for different charges. Our observations are similar to those reported by Ghorai and Yashonath [**?**]. We find that above a certain value of charge the diffusion value as a function of solute size shows a nonmonotonicity and a diffusivity maximum arises. The appearance of the maximum not only depends on the magnitude of the charge but also on the sign (+ve or -ve) of the charge and the temperature of the system (not shown here). The dependence on the sign of the charge tells us that the water structure near +ve and -ve charges are different, which has been reported earlier [**? ?**]. We next, keep the q_s constant (q_s=0.05e) and change the LJ interaction strength. Note that for these interaction values the LJ interaction alone does not produce any nonmonotonicity in the range of σ_{sO} values studied here. However, as seen in Fig. 2c in the presence of charge there appears a nonmonotonicity.

If we now compare the size dependent diffusion anomaly as observed in the case of charged (Fig. **??**) and neutral (Fig. **??**a) solutes, we find that (i) for charged solutes with an increase in charge the peak of the diffusivity maximum shifts to larger solute sizes and with an increase in ϵ_{sO} it shifts to smaller solute sizes. In the case of neutral solutes with an increase in ϵ_{sO} it remains fixed, (ii) for charged solutes the enhancement of diffusion decreases with an increase in interaction (both ionic and nonionic) whereas the opposite trend is observed neutral solutes. We also find that the range of sizes where the diffusivity maximum is present is different for the charged and the neutral solutes. Thus although both charged and neutral solutes show a nonmonotonicity in size dependence of diffusion, the nature of the nonmonotonicity is different.

Interplay between LJ and Coulombic interaction

In this section, we show that all the features observed for the charged solute diffusion can be explained in terms of the interplay between LJ and Coulombic interactions.

There is a basic difference in the way the interaction potential changes with size for charged and neutral solutes. For neutral LJ solute, the shape of the potential remains the same but its range shifts with solute-water diameter. In case of a charged solute both Coulombic and LJ interactions are present. The LJ part is size dependent, but the Coulombic part is not. This leads to a change in both the shape and the range of the potential as a function of the solute-water diameter. This shape and range further changes with the solute-water interaction and charge on the solute. To analyze this effect we plot the average per particle potential energy and its components, the Φ_{pot}^{LJ} and Φ_{pot}^{Coul} for some representative values of q_s (Fig. **??** and Fig. 4.10 and Fig. 4.11a in Appendix I) and some ϵ_{sO} values (Fig. **??** and Fig. 4.11b in Appendix I).

We show that for charged solutes, at large sizes, the potential is primarily dominated by the LJ part. This is precisely the reason the diffusion coefficient for the large sizes are similar to that of the neutral solutes (Fig. **??**). As the solute size decreases the charge density of the solute increases and the Coulombic part dominates over the LJ part. For most cases, this leads to a crossover as a function of solute size from the LJ dominated to the Coulomb dominated regime as shown in Fig. **??**. As we increase the charge on the solute, due to an increase in charge density the crossover to the Coulomb dominated regime takes place at a larger solute size leading to a shift of the crossover to higher sizes. If we now increase the ϵ_{sO} value keeping q_s constant the strength of the LJ interaction increases leading to a shift of the crossover to smaller solute sizes as seen in Fig. **??**. As shown in Fig. **??** and Fig. **??** whenever there is a crossover it gives rise to a nonmonotonicity in the potential energy. The diffusivity maximum appears to be a causal effect of this nonmonotonicity in the potential energy. Note that, for systems where there is no crossover the potential energy is monotonic (Fig. **??**) and also there is no diffusivity maximum.

Although we claim that the nonmonotonicity in potential energy and diffusivity are connected, the position of the peaks may not be identical. In comparison to the potential energy peak in some cases, we do see a marginal shift of the diffusivity peak to smaller solute sizes. This is because diffusion is not only determined by the potential energy but also by the size of the particle. Initially, the potential energy increases with decreases in size and thus both potential energy and solute size facilitate the diffusion process. However, after a certain size when the potential energy decreases with a decrease in size then they act in the opposite direction. The former hinders the diffusion process and the latter facilitates it. This competition can lead to a shift in the diffusivity maximum to smaller solute sizes. Eventually when the potential energy has a large negative value then it wins over the size dependence and the diffusion seems to be determined predominantly by the potential energy. Thus, our analysis clearly shows that for the charged solutes the nonmonotonicity in the potential energy arising from the interplay between the LJ and the Coulombic parts is a prerequisite for obtaining a nonmonotonicity in the diffusion. For neutral solutes above a certain value of the solute-water interaction we do find a diffusivity maximum, but no such nonmonotonicity.

Next, we analyze the second point, i.e. the decrease in the peak value as a function of solute charge and solute-water interaction strength. We find that for systems where the charge is increased, keeping the LJ interaction constant, the diffusivity maximum shifts to larger sizes and corresponding smaller diffusion coefficients. For systems where the LJ interaction is increased keeping the charge constant this reduction in the peak value is an effect of stronger LJ interaction.

Although both positively and negatively charged solutes show a diffusivity maximum there are some subtle differences. The diffusivity maximum for the negatively charged solute appears at a lesser value of solute charge compared to the positively charged solute. Also for the model systems where both the type of charges show a diffusivity maximum, the one for the negatively charged solute appears at a larger solute size when compared to that of the positively charged solute. This is similar to the observations made in experimental studies [**?** **?** **?**] and earlier simulation study of real ions [**?**]. Here we show that this shift in the position of the diffusivity maximum is accompanied by the shift of the crossover from the LJ to the Coulomb dominated regime (compare Fig. **??** in the main text with Fig. 4.10 in the Appendix I). Thus our model study suggests that for the same value of charge and solute size, the negatively charged solute can stabilize more from the Coulomb interaction compared to the positively charged solute. This is because the positively charged solute faces a steric hindrance while approaching the Oxygen atom whereas the negatively charged solute does not face any such hindrance while approaching the Hydrogen atom.

As discussed earlier, for systems where both ionic and nonionic (in this case LJ) interactions are present, the variation of charge renormalizes the effect of LJ interaction and vice versa [**?**]. Here we find that the increase in charge has a weaker effect on the LJ dominated regime (Fig. 4.11a in Appendix I), however the increase in ϵ_{sO} has a stronger effect on the Coulomb dominated regime (Fig. 4.11b in Appendix I). In the LJ regime, the value of Φ_{sw}^{LJ} doesn't change much with q_s whereas the value of Φ_{sw}^{Coul} increases with ϵ_{sO} *i.e.* effect of Coulombic attraction reduces. This can be understood from the solute-Oxygen radial distribution function, $g_{sO}(r)$ (Fig. **??**). We compare the $g_{sO}(r)$ for two different ϵ_{sO} values. This is done for two representative solute sizes, one where the LJ interaction is dominant (larger solutes) and the other where the Coulombic interaction is dominant (smaller solutes). For larger solute sizes the $g_{sO}(r)$ peak remains at the same position and the peak becomes sharper with an increase in ϵ_{sO}. However, for smaller solute sizes where the Coulombic interaction dominates the scenario is different. Here, with the increase in ϵ_{sO} the $g_{sO}(r)$ peak value reduces and the peak shifts to a higher value of 'r'. As the ϵ_{sO} increases, the steric hindrance at smaller 'r' due to the LJ interaction increases sharply leading to the shift in $g_{sO}(r)$. This finally leads to a weaker effect of the Coulombic part. This effect of LJ interaction on the Coulomb dominated regime should also depend on the q_s value and the effect is expected to decrease with the increase in q_s. Interestingly with an increase in q_s the width of the Coulomb dominated regime increases (*i.e.* it starts from a larger solute size) whereas with the increase in ϵ_{sO} the width of the LJ dominated regime does not change much. From the analysis of the solute-Oxygen radial distribution function we suggest that for systems where the nonionic interaction is given by a LJ kind of potential, the hydrophilicity of the solute will also depend on the strength of this potential. For solutes having the same charge the one that has stronger nonionic interaction will be less hydrophilic.

Ordering of water around the ions

In this section, we study both orientation of water molecules and the stability of the water solvation shell around solute particles. We chose systems where ϵ_{sO}=1.58 kJ/mol and solutes charges q_s=0.05e, 0.3e and 1.0e. For each value of charge we take two different solute sizes, one which is in the LJ dominated regime (2.5 Å for both $q_s = 0.05e$ and $q_s = 0.3e$ and 5.5 Å for $q_s = 1.0e$) and the other which is in the Coulomb dominated regime (1.5 Å for $q_s = 0.05e$, 1.9 Å for $q_s = 0.3e$ and 2.3 Å for $q_s = 1.0e$). As seen from Fig. 3 these regimes are dependent on q_s values and so are the solute sizes. For comparison, we also study the system where the solute is neutral.

Orientation: We analyze the probability distribution of first shell water orientation $P(\theta)$, around solute particles where θ is the angle between the vector bisecting the water molecule w.r.t the vector connecting the water Oxygen to the solute (Fig. **??**). We find that for larger solutes, in the LJ dominated regime, the probability distributions are similar for the -ve and +ve solutes. We further find that they are also similar to that obtained for a neutral solute (also see Fig. 4.10a in the Appendix I). For these systems, there is a broad distribution with a peak around 100 degree (Fig. **??**a, Fig. **??**c and Fig. **??**e). This kind of distribution is usually obtained when the water orientation around the solute is determined by the water-water hydrogen bonding[**?** **?**]. For smaller solutes in the Coulomb dominated regime we find some finite peaks and as expected, these peak positions are different for the +ve and the -ve solutes. These peaks also become sharper with an increase in the charge. This shows that for these solutes some of the water molecules participate in the solvation process and the orientations of those water molecules are fixed at certain angles and dominated by the solute-water ionic interaction. The position of the peak and the observation that peak becomes sharper with an increase in charge density is similar to that reported earlier for real ions [**?** **?** **?**] (Fig. **??**b, Fig. **??**d and Fig. **??**f). These $P(\theta)$ distributions obtained in this study can explain observations made earlier by Lee and Rasaiah[**?**]. In their simulation study of cations in water they found that the water in the first shell around a bigger size cation, Cs^{+} does not have any specific orientation, whereas around a smaller size cation, Li^{+} some of the water dipoles are oriented towards the cation.

Neighbour shell rearrangement: In this section we study the effect of solute charge and size on the neighbour/solvation shell rearrangement dynamics. For this we first plot the trajectory of coordination number N_c, which is the number of water molecules in the first neighbour shell of the solute, *i.e.* within the first peak of the solute-water RDF. Like orientation, we compare the solvation shell dynamics of charged (both +ve and -ve) and neutral solutes. As shown in Fig. **??** for charged solutes which are in the LJ dominated regime (larger size) the solvation shell shows large fluctuations and this is similar to that found for a neutral solute of the same size. For charged solutes which are in the Coulomb dominated regime (smaller size), the solvation shell is stable and the N_c trajectory is different from that of a neutral solute of the same size which shows large fluctuations. These observations made here are coherent with the simulation results of residence time correlation function of first shell water molecules around cations [**?**].

We also calculate the normalized variance in the coordination number, $\kappa = \frac{<N_c^2>-<N_c>^2}{<N_c>}$ which is related to the local compressibility [**?**]. The values are given in Tables 1 and 2. For both sets of data ($q_s = \pm 0.3$ and $q_s = \pm 1.0$) κ values are less for solutes in the Coulomb dominated regime compared to those in the LJ dominated regime. When we compare the κ values for -ve and +ve charges we find that for the same size they are less for -ve charges. We also find that κ values for solutes in the LJ dominated regime are similar to that of neutral solutes of the same size and the value increases with size. For comparison, we calculate the bulk water κ by computing the coordination number fluctuation in a hydration shell shaped volume around an arbitrary point in bulk water [**?**]. The κ value for bulk water is 0.26 corresponding to a solute with $\sigma_{sO} = 2.5\mathring{A}$ and 0.28 corresponding to a solute with $\sigma_{sO} = 5.5\mathring{A}$. Thus for large neutral solute or solute in the LJ dominated regime the κ value is either the same or higher than that of bulk water. This observation is similar to that reported earlier [**? ?**].

$\sigma_{sO}(\mathring{A})$	$q_s = 0e$	$q_s = +0.3e$	$q_s = -0.3e$
1.9	0.21	0.16	0.10
2.5	0.25	0.22	0.21

Table 4.1: Normalized variance in the coordination number, $\kappa = \frac{<N_c^2>-<N_c>^2}{<N_c>}$, for $q_s = \pm 0.3e$

$\sigma_{sO}(\mathring{A})$	$q_s = 0e$	$q_s = +1e$	$q_s = -1e$
2.3	0.22	0.13	0.11
5.5	0.59	0.52	0.51

Table 4.2: Normalized variance in the coordination number, $\kappa = \frac{<N_c^2>-<N_c>^2}{<N_c>}$, for $q_s = \pm 1e$

From the study of the water orientation and also the neighbour shell fluctuation, we find that the water molecules around a solute in the Coulomb dominated regime are strongly bound to it and the solute probably behaves like a water structure maker, *i.e.* kosmotrope [**? ?**]. On the other hand, the solute in the LJ dominated regime behaves like a neutral hydrophobic solute. Although, we find that compared to bulk water the κ values are higher for some of the solutes (like for $\sigma_{sO} = 5.5\mathring{A}$) suggesting that the water structure around them is more flexible, we are hesitant to call them water structure breaker, *i.e.* chaotrope. This is because other studies have shown that water around a hydrophobic solute, smaller than a nanometer, maintains bulk like structure and there is a size dependent order-disorder transition around one nanometer [**? ?**]. Moreover, Yethiraj and coworkers have shown that simulation studies using similar ion-water models fail to show the structure breaking properties of certain salts which are experimentally known to have chaotropic properties[**?**].

Excess entropy and diffusion

The connection between the excess entropy and the anomalies in the diffusivity plot is demonstrated here. The excess entropy is evaluated using a fairly accurate structural information in form of pair correlation function. At the same temperature (T) and density (ρ) the excess entropy (S_{ex}) is defined as the difference between total entropy (S) and ideal gas entropy (S_{id}). Also, S_{ex} can be expanded in an infinite series or a multi-particle correlation expansion, as, $S_{ex} = S_2 + S_3 + ...$ using Kirkwoods factorization function. Here, S_n is the n body contribution to the entropy. The main contribution in excess entropy comes from the pair excess entropy S_2. For a binary system at temperature (T) the pair excess entropy S_2 can be written in terms of the partial radial distribution functions [**?**](ref 35 in JCP 125, 204501),

where $g_{\alpha\beta}(r)$ is the atom-atom pair correlation between atoms of type α and β, k_B is the Boltzmann constant, N is the total number of particles and x is the mole fraction of component in the mixture.

To analyze a corresponding state relationship between diffusivity and the excess entropy, we plot the S_2 against 1/σ_{sO} in Fig. **??**. The peak positions in the entropy plot show a similar trend like the diffusion plots in Fig. **??**. Excess entropy values are higher when the particles are moving faster and vice versa. Increasing charge, the maxima of the peak value in the diffusion plots shift to bigger sized solute particles. That shift is reflected in entropy values also. In the inset of Fig. **??**, we have plotted the logarithm of the diffusivity ($\ln D$) against the corresponding excess entropy and we see almost linear relationship between them, which is in good agreement with the observations noted in some earlier studies[**? ?**].

4.4 Conclusion

In this work, we do a comparative study of the size dependence of diffusion for both charged and neutral solutes in water. Both the type of systems show a size dependent diffusivity maximum. However, the nature of the maximum as a function of interaction strength is different for the neutral and the charged solute systems. For the neutral solute system the position of diffusivity maximum is independent of solute-water interaction, whereas for the charged solute system with an increase in solute-water interaction the maximum shifts to smaller solute sizes and with an increase in solute charge it shifts to larger solute sizes. We also find that for charged solutes the height of the maximum decreases with an increase in the interaction strength and increase in the charge. This is different from that observed for neutral solutes.

We show that for charged solutes with a decrease in the solute size, there is a cross over from the LJ dominated to the Coulomb dominated regime. This interplay between the LJ and the Coulomb interactions leads to a nonmonotonicity in the potential energy. We further show that this nonmonotonicity in the potential energy is a prerequisite for obtaining the diffusivity maximum. Earlier studies on real systems have connected the diffusivity maximum to the interplay between the nonionic and ionic interactions [**? ? ? ? ? ? ? ? ? ? ? ?**]. However, as far as our knowledge this is the first time it is shown that this leads to a nonmonotonicity in the potential energy which is then connected to the nonmonotonicity in diffusion. Although we claim that the potential energy has a LJ and a Coulomb dominated regime, they are not completely independent of each other. Our study shows that the effect of the charge is weak in the LJ dominated regime however the strength of the LJ interaction has a strong effect on the Coulomb dominated regime. It also suggests that the nonionic interaction strength will play a role in determining the degree of hydrophilicity of an ionic solute. The increase in strength of the nonionic interaction will make a charged particle less hydrophilic. Similarly, other observations made here can be helpful in modeling force fields.

We further show that the probability distribution of orientation of the water molecules around a charged solute depends on whether the solute is in the LJ dominated regime or in the Coulomb dominated regime. For solutes in the LJ dominated regime the probability distribution is independent of the sign of the charge and also similar to that found around a neutral solute. The probability distribution, in this case is determined by the water-water hydrogen bond. However, when the solute is in the Coulomb dominated regime the probability distribution is different with peaks at certain angles suggesting that the water orientation is dominated by the solute-water ionic interaction and some water molecules are oriented in a specific way to solvate the ion. As expected, the distribution is also different for the +ve and the -ve charges.We also study the normalized variance in the coordination number for solutes in the LJ and Coulomb dominated regime, and for bulk water. We find that the κ values broadly follow the order- large neutral solutes or solutes in the LJ dominated regime > bulk water > solutes in the Coulomb dominated regime. The higher the κ value the more compressible is the system and also the water is less structured. However, it appears that within the range of solute sizes studied here, identifying water structure breakers are tricky [**? ? ?**]. A recent coarse-grained model study where the ion-water interaction was modeled using the concepts of ion solvation energy was able to reproduce the experimental results, predicting chaotropic, water structure breaking behaviour of the solutes [**?**]. In this work to identify the solutes in the LJ dominated regime as water structure breaker we need to study the water dynamics as a function of solute concentration, which will be taken up in the future.

4.5 Appendix

These are few additional figures related to ordering of water around neutral solute particles and potential entropy plots for positive solute particles.

CHAPTER 5

Fickian Yet Non-Gaussian Behaviour: A Dominant Role of the Intermittent Dynamics

> "The chief reason for going to school is to get the impression fixed for life that there is a book side for everything."
>
> *Robert Frost*

5.1 Introduction

We present a comparative study of size dependence of diffusion for charged and neutral solutes in water. Although both show nonmonotonicity of the size dependence of diffusion, their nature and origin are quite different. For neutral solutes, the peak position and the value of diffusion at the maximum are both independent of the solute-water interaction. Interestingly, for charged solutes, with an increase in solute-water interaction strength the peak position shifts to lower solute sizes and with an increase in charge, it shifts to higher solute sizes. The diffusion value at the peak reduces with an increase in both solute-water interaction and solute charge. We show that all these features observed for charged solutes can be understood in terms of the interplay between ionic and nonionic interactions which is definitely absent for neutral solutes. Some of the earlier studies addressing the nonmonotonicity in diffusion did suggest the interplay between the two interactions to be the cause. However, this is the first time we show that such interplay gives rise to the nonmonotonicity in the potential energy which is a prerequisite for obtaining the nonmonotonicity in the diffusion. Such nonmonotonicity in the potential energy is absent for neutral solutes.

The next section contains simulation details. Section 3 contains the results and discussion followed by the conclusion in section 4.

5.2 Simulation Details

In this work we perform an equilibrium Molecular Dynamics (MD) simulation with an atomistic model where particle type 'i' is interacting with particle type 'j'with truncated and shifted Lennard-Jones (LJ) pair potentials, given by

Where is the distance between pairs, for Week Chandler Anderson (WCA) system [**?**] and ${r_{ij}}^{c} = 2.5\sigma_{ij}$ for LJ system. Here $i, j = 1, 2$, where 1 refers to solvent and 2 refers to solute. For all the systems we consider that the interaction between the solvent and the solute has a soft core which allows inter-penetration between solute-solvent pair.

We take a system with 1000 particles where 10 of them are solutes and rest are solvents. In this simulation we study different systems varying the interaction potential (both attractive and repulsive), solvent mass and the interspecies interaction length.

We have done isothermal-isobaric ensemble (NPT) simulation at a reduced temperature 1.663 (initially the crystals are melted in a higher temperature, later it is cooled down) and at reduced pressure 7 where the average density of the system is 0.8867 which ensures a crowded environment.

The MD simulations are performed in a cubic box using Nosé-Hoover thermostat and barostat [**? ?**]. The integration step is 0.001τ, where $\tau = \sqrt{\frac{M\sigma_{11}^2}{\varepsilon}}$, where the solute mass $M = 1$. In this study, length and temperature are given in the units of , σ_{11} and $\frac{k_BT}{\varepsilon}$. We consider solvent mass, 'm', over a wide range, 0.5,1,10 and 100 for both attractive and repulsive systems. σ_{11} is taken as 1, σ_{22} is .171 and $\sigma_{12} = \sigma_{22} + .171$. All the above mentioned systems are equilibrated for 1-2 ns followed by a production run of 4 ns (in Argon units). Systems with larger mass are equilibrated

Table 5.1: Solute, solvent diffusion values D_1 and D_2 respectively and their ratio D_2/D_1 for different systems. In every system ϵ_{11} is 1 and ϵ_{22} is 0.5.

system	solvent mass (m)	ϵ_{12}	D_1	D_2	D_2/D_1
LJ	0.5	6	0.119	.5	4.2
LJ	1	6	0.08	.35	4.375
LJ	10	6	0.0278	.23	8.27
LJ	100	6	0.0088	.207	23.5
LJ	100	2	0.0087	1.5	172.41
LJ	100	4	0.0084	.44	52.4
LJ	100	16	0.0086	.02	2.33
LJ	100	24	0.0087	.016	1.84
WCA	100	1	0.0087	1.6	183.90

over longer times.

We perform Molecular Dynamics (MD) simulations using LAMMPS package [**?**].

5.3 Results and Discussion

In this study we work with a solute-solvent system where the solute size is chosen to be small so that the solute can explore the inter-solvent cage [**?**]. In earlier studies [**? ?**] it has been shown that for such small solute particles the non-Gaussian behaviour of the van Hove correlation function is due to decoupling in solute-solvent dynamics. In order to understand how slowing down of solvent dynamics, which leads to the decoupling, effects the solute motion, we study a set of systems where we vary the solvent mass. As observed earlier [**? ?**] with the increase in solvent mass the decoupling between the solute and the solvent dynamics increases as seen from the D_2/D_1 values in Table 1. In these studies the solute-solvent interaction is kept moderately attractive (ϵ_{12}=6). The mean square displacement (MSD) is calculated from single particle trajectory, r(t), and then time averaging and also particle averaging is performed,

Here, T is the overall measurement time, N is the number of particle, which is 10 in our case. The MSD of the solute in all the systems are linear with time and for higher solvent mass the linear region sets in at an earlier time as has been observed in previous studies [**?**] (Fig.**??**). A possible reason for this observation can be, for large solute-solvent decoupling solute does not expect the solvent to have any dynamics thus the diffusive dynamics for the solute in these systems sets in at earlier assuming the solvent to be static. The linearity of the MSD predicts that the motion is diffusive. The van Hove correlation function which is the distribution of probability displacement ($G_s(r,t) = \frac{1}{N}\langle\sum_{i=1}^{N}\delta(r + r_i(0) - r_i(t))\rangle$), is calculated at the time where the MSD is linear and $< \triangle r^2(t) >$= 18. Although the MSD is linear the $G_s(r,t)$ shows non-Gaussian nature (Fig.**??**). In order to check the ergodicity of the system we also calculate the mean square displacement from the probability distribution. The mean squared displacement can be expressed as the second moment of van Hove correlation function,

Using Eq. **??** we calculate MSD at few points which are shown as open circles in Fig.**??**. We find that the MSD obtained using both the methods are identical indicating the systems to be ergodic. Thus we have a set of ergodic systems which show Fickian and non-Gaussian dynamics.

We show in Fig.**??**a that the non-Gaussian behaviour of $G_s(r,t)$ increases with the increase in solvent mass. In order to measure the departure from Gaussianity we also plot $P(log_{10}(r;t)) = 4\pi r^3 ln(10) G_s(r,t)$ (Fig.**??**b). When the van Hove function is Gaussian then the peak value of $P(log_{10}(r,t)) \simeq 2.13$ [**?**]. It's decrease in value is a measure of the degree of departure from Gaussianity. The departure from Gaussian behaviour is pronounced in Fig.**??**. As expected, comparing figures Fig.**??**(a) and (b) we find that systems which show larger departure from Gaussianity in the former, has smaller peak values in the latter. We find a positive correlation between the departure from Gaussianity and decoupling of solute-solvent dynamics which is similar to what has been reported earlier [**?** **?**]. It has been argued that although the solute reaches a diffusive dynamics, due to slow solvent dynamics it is unable to explore different solvent environments thus leading to the non-Gaussian behavior of the probability distribution. It is found that for such systems the van Hove correlation function at later times, which is long enough to explore the ergodic solvent dynamics, is Gaussian. Although our results apparently look similar to that observed in earlier studies, for our systems with large solvent mass we do not obtain the Gaussian behaviour even when the van Hove correlation function is calculated at about 70 times τ_α, where τ_α is the α relaxation time of the solvent (Fig.**??**).

Note that for attractive solute-solvent interaction and large solvent mass we not only have the decoupling of the dynamics but the solute motion also becomes intermittent. The second peak or the shoulder in the $P(log_{10}(r,t))$ plot is a signature of this intermittency which is observed for m =10 and 100 (Fig.**??**(b)). We believe that for certain systems both, this intermittency and the decoupling, contribute to the non-Gaussian van Hove correlation function. In order to understand their independent contribution we study a system where the solute-solvent interaction is repulsive in nature. For repulsive solute-solvent interaction although the decoupling in dynamics exists [**?**] the solute dynamics is not expected to be intermittent. We find that similar to the LJ systems the van Hove correlation function and $P(log_{10}(r,t))$ plots (calculated at a time where $< \triangle r^2(t) >$≈920) show a larger departure from Gaussianity when the solvent mass increases (Fig.**??**). However note that compaired to the LJ systems the departure form Gaussianity is much weak for the WCA systems. In Fig.**??** we show the time evolution of $P(log_{10}(r,t))$ for $m = 100$, which shows maximum departure from Gaussianity at short times. Unlike for the case of attractive solute-solvent interaction the probability distribution becomes Gaussian at longer times and the $P(log_{10}(r,t))$ does not show any bimodal behaviour. From the absence of the double peak in $P(log_{10}(r,t))$ we may conclude that as expected, the WCA system does not have intermittent dynamics. Note that by changing the solute-solvent interaction the structure and dynamics of the solvent remains almost unchanged. As a representative plot we show the overlap function of the solvent when $m = 100$ for both WCA and LJ systems (Fig.**??**). We also show the corresponding solvent structure factor in the inset of Fig **??**. Thus the difference in behaviour between the LJ and WCA systems is not due to the solvent structure or dynamics but due to the difference in the solute dynamics. In one case (LJ systems) the solute dynamics is intermittent and in other case (WCA systems) it is not.

The intermittency in the solute motion appears quite similar to that found in supercooled liquids. In supercooled liquids there is formation of domains which give rise to the intermittency. In our present system there is no domain formation and the intermittency is the effect of attractive solute-solvent interaction. While undergoing random walk, the solute explores the transient solvent cage [**? ?**]. As the solute is small when it passes through the neck of the cage it feels uneven attraction from the different solvent particles and spends longer time near a particular solvent, which can be envisaged as a sticky point and leads to the intermittency in the solute dynamics. Thus we may expect that larger the attraction the more intermittent is the dynamics. In order to understand the connection between solute-solvent interaction, intermittency and non-Gaussianity of $G_s(r,t)$ we study a series of system by varying the strength of the solute-solvent interaction from repulsive to highly attractive (Fig.**??**). In all these cases the solvent mass is kept at 100 where the LJ system (ϵ_{12}=6) shows maximum deviation from Gaussianity. Our next analysis reveals that for LJ systems the non-Gaussianity is a combined effect of dynamical decoupling and intermittent solute dynamics and it has a non-monotonic dependence on the solute-solvent interaction strength. While the decoupling decreases with increasing strength of interaction the intermittency shows a non-monotonic dependence on the same and this gives rise to non trivial results.

For repulsive and small attractive interaction there is a large decoupling between the solute and the solvent dynamics as seen from the D_2/D_1 values in Table 1. However the time evolution of $P(log_{10}(r,t))$ does not show any bimodal nature thus predicting no strong intermittency in the solute dynamics. Thus, although the large solute-solvent decoupling initially gives rise to non-Gaussian $G_s(r,t)$, at longer times it becomes Gaussian as seen in Fig.**??** for WCA system and Fig.**??**a for LJ system with ϵ_{12}=2. On the other hand, for very large solute-solvent interaction ($\epsilon_{12} > 6$) the decoupling of the solute and the solvent dynamics reduces as seen from the D_2/D_1 values in Table 1. Similar to the repulsive and small attractive systems, the time evolution of $P(log_{10}(r,t))$ does not show any bimodal nature thus the intermittency in the solute dynamics is also not present. Hence the dynamics remains almost Gaussian for short, intermediate and long times (Fig.**??**). However, for intermediate solute-solvent interaction ($2 < \epsilon_{12} < 12$) there is strong enough decoupling between the solute and the solvent dynamics (Table 1) and strong intermittency in the dynamics as observed in the clear bimodal behaviour of the time evolution of the $P(log_{10}(r,t))$ (Fig.**??** and Fig.**??**b). In these two cases till about $70\tau_\alpha$ the dynamics is non-Gaussian. Note that in all these systems the timescale of the solvent dynamics are similar as seen from diffusion values in Table 1 and the overlap function in Fig.**??**. Thus if the non-Gaussian behaviour is only due to the slow solvent dynamics then the recovery of the Gaussian nature should happen over the same time period, which does not appear to be the case. Note that for all the systems the $P(log_{10}(r,t))$ is plotted till about $70\tau_\alpha$. Thus our study predicts that in crowded systems at least there are two different sources of non-Gaussian behaviour. One is the difference in timescale of the solute and solvent dynamics and the other is the intermittency in the solute dynamics which arises for attractive solute-solvent interaction. In the first case where there is just dynamical decoupling, the Gaussian nature is recovered at longer times, however in the second case where along with the dynamical decoupling there is also intermittency in the solute dynamics, the non-Gaussian nature remains even at about $70\tau_\alpha$. For ϵ_{12}=4 and 6 we do find that although around $70\tau_\alpha$ the non-Gaussian behaviour as seen in the $P(log_{10}(r,t))$ plot still persists the intermittency in the dynamics starts to disappear. For these two systems we calculate the $P(log_{10}(r,t))$ till longer times ($3565\tau_\alpha$ for both ϵ_{12}=4 and 6) and find that eventually the dynamics appears to become close to Gaussian (Fig.**??**). However note that in these two cases the recovery of the Gaussian nature is not due to long averaging over solvent dynamics but the dissappearance of intermittency.

Let us compare between the WCA and LJ (ϵ_{12}=6) systems when mass=100. Note that the WCA system shows larger decoupling of the solute-solvent dynamics (Table 1). However if we compare the $P(log_{10}(r,t))$ plots (Fig **??** and **??**) we find that the LJ system, which also has intermittency in its dynamics, shows larger departure from Gaussianity. Along with this we find that for the LJ system the non-Gaussian nature also persists for longer times. Thus the study reveals that intermittency in the solute dynamics provides a dominant contribution to the non-Gaussian nature of $G_s(r,t)$.

However, note that just attractive solute-solvent interaction is not sufficient to give rise to intermittency. For small ϵ_{12} values although there is decoupling but the interaction is not strong enough to produce intermittency. For large ϵ_{12} values the solute dynamics cannot decouple from the solvent dynamics. Only for intermediate ϵ_{12} values the strength of the interaction is such that there is enough decoupling between the solute and the solvent dynamics and also enough attraction between the two species.

5.4 Conclusion

When the dynamics of a particle is Brownian it is supposed to have Gaussian distribution of its displacement probability (van Hove correlation function) which eventually gives rise to Fickian diffusion where the MSD remains linear with time. However there are systems where although the diffusion is Fickian the distribution of displacement probability is non-Gaussian. This anomaly has been explained as an effect of different phenomena like weak ergodicity breaking [**?**], decoupling of solute-solvent motion [**? ?**] and diffusing diffusivity [**? ?**]. In order to further understand this Fickian but non-Gaussian dynamics in this work we study a wide range of solute-solvent systems where the solute size is kept small so that it can explore the inter solvent cage and mimic the diffusion in a crowded environment. The mass of the solvent is varied to study the effect of the solute-solvent dynamical decoupling on the solute motion and the solute-solvent interaction is also varied to study the effect of it on the solute dynamics.

We find that similar to that reported earlier as the decoupling of the solute and the solvent dynamics increases the van Hove correlation function becomes more non-Gaussian [**? ?**]. However, for repulsive and weak attractive values of solute-solvent interaction the dynamics becomes Gaussian when averaged over long enough time so that the solute explores all possible solvent environments. For these systems the origin of the non-Gaussian dynamics is the solute-solvent decoupling. We find that apart from this there is at least one more phenomena, the intermittency in the solute dynamics, which gives rise to non-Gaussian nature. Intermittency in particle dynamics, also giving rise to non-Gaussian dynamics, is usually reported in supercooled liquids [**?**]. The origin of this intermittency is the formation of dynamically heterogeneous domains. In our system there is no such domain formation and the intermittency is an effect of attractive interaction between the solute and the solvent. Surprisingly the intermittency is maximum for intermediate solute-solvent attraction and reduces substantially when the solute-solvent attraction is decreased or increased. The reason behind this is to produce intermittency the attraction on one hand should be weak enough to have decoupling in the solute-solvent dynamics and on the other hand strong enough to produce sticky points in the solute path. In case of intermittent dynamics the non-Gaussian behaviour persists over a longer time.

Thus our study reveals that for diffusion in a crowded environment for certain range of attractive interaction between the solute and the solvent it is possible to have intermittency in the dynamics and this can play a dominant role in giving rise to the non-Gaussian but Fickian dynamics.

CHAPTER 6

Summary and Future Work

“My long two-pointed ladder’s sticking
through a tree
Toward heaven still,
And there’s a barrel that I didn’t fill
Beside it, and there may be two or three
Apples I didn’t pick upon some bough.
But I am done with apple-picking now. ”

Robert Frost,
After Apple-Picking

The anomalies in diffusion still remains a problem yet to be completely solved. We have learned about size dependence in anomalous diffusion in ionic[**? ? ? ? ? ? ? ? ? ? ?**] and neutral solutes[**? ? ? ? ? ? ?**]. Besides these works, numerous theories have been proposed to explain the non-Gaussianity of the van Hove function or distribution of displacement when the diffusion is fickian [**? ? ? ?**].

In the first chapter we have introduced some of the important concepts and the existing problems regarding different types of diffusion anomalies.

We have discussed all the methods and mathematical tools used in our work in the next chapter.

In the third chapter we have introduced a model to predict the diffusion of neutral solutes which are smaller in size than the solvent and interacts with the solvent via a repulsive potential. We have shown how the departure from SE prediction changes with change in solute-solvent interaction. We have predicted the formation of transient solvent cages and explained how the timescale of these transient cages contributes to the diffusion anomaly. We have modeled the diffusion of the solute in the solvent as a combination of viscous diffusion and cage diffusion and have shown that the model correctly predicts the contribution of these two diffusions in different environments. Our study shows that decoupling between solute solvent dynamics is essential for the solvent to explore these cages. The more stable the cages appears to the solvent, the more the cage diffusion contributes to the total.

After studying the anomalous diffusion for neutral solutes, in the following chapter, we have introduced the Coulombic interaction in our system and we have elaborated the discussion about the trend of size dependency of diffusion anomaly for the charged solutes in water.

In this work, we have extensively studied the role of interplay between Coulombic and LJ interaction potential in explaining this diffusion anomaly. We have shown that as a function of solute size there are two different regimes, one where the interaction is dominated by the LJ potential and the other where the interaction is dominated by the Coulombic potential, We have also discussed the orientation of water molecules around the solute particles of various charge and size. We have also checked the stability of the solvation shell and it's dependency on the solute size. Both the orientation and the solvent shell stability predicted the presence of two different regimes which are dominated by the two different kinds of interactions.

Similarly, to identify the solutes in the LJ dominated regime as water structure breaker we need to study the water dynamics as a function of solute concentration, which can be taken up in the future.

When the dynamics of a particle is Brownian it is supposed to have Gaussian distribution of its displacement probability (van Hove correlation function) which eventually gives rise to Fickian diffusion where the MSD remains linear with time. However there are systems where although the diffusion is Fickian the distribution of displacement probability is non-Gaussian. This anomaly has been explained as an effect of different phenomena like weak ergodicity breaking [**?**], decoupling of solute-solvent motion [**? ?**] and diffusing diffusivity [**? ?**].

However, in our study, we have shown that for repulsive and weak attractive values of solute-solvent interaction the dynamics becomes Gaussian when averaged over long enough time so that all possible solvent environments are explored by the solutes. For these systems, the origin of the non-Gaussian dynamics is the solute-solvent decoupling. We find that, apart from the solute-solvent decoupling, there is at least one more phenomena, the intermittency in the solute dynamics, which gives rise to non-Gaussian nature. Unlike in supercooled liquids the origin of this intermittency is not the formation of dynamically heterogeneous domains. We show that this intermittency arises due to solute-solvent interaction and is maximum for intermediate solute-solvent attraction. This study can be realized in more realistic systems like bio-polymer filaments, lipids and other biological systems where there is a range of interactions present between the tracer particle and the media.

Diffusion of smaller particles in a crowded environment is potentially much larger topic to discuss. How pesticides or herbicides goes through the pores in the soil and mix with the groundwater, how a sunscreen lotion takes care of our skin or how a drug molecule enters into a cell through the lipid bilayer, all these real life fundamental problems are commonly associated with a single topic, dynamics of a tracer particle when the solvent viscosity is high. From diffusion in carbon nanotube to diffusion through zeolite, the SE relation is either valid or it is not followed. In this entire work, we tried to predict and measure all different types of diffusion anomalies. However, I still believe it is not enough. There are more colorful doors to be opened.

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