

## Diffusion coefficient of ionic solvation shell molecules

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It is shown that, for a tightly bound ion-solvation shell complex, the mean square displacement for solvation molecules is characterized by a long lasting transitory. This initial portion is related to the rotational relaxation of the complex and can reach up to several hundred picoseconds for a representative example such as the  $\text{Mg}^{2+}$  ion in water. As the diffusion coefficient is usually fitted using much shorter time spans, unnoticed overestimations are possible. It is argued that, instead of computing the aforementioned diffusion coefficient from the mean square displacement, it should be defined taking as a basic guideline the ratio between the rotational relaxation time of the complex and the lifetime within the first solvation shell. © 2005 American Institute of Physics.

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### I. INTRODUCTION

Diffusion of molecules belonging to the ionic solvation shell has been studied for a variety of systems in the liquid phase.<sup>1–16</sup> Generally, their motion is found to be substantially slowed down with respect to bulk solvent molecules but still somewhat faster than that of the ion. This conclusion is usually founded on the computation of the diffusion coefficient for the subset of first solvation shell molecules: its value is larger than that of the ion and lower than that of the bulk. While a hindered motion seems perfectly reasonable on physical grounds, in this work it will be argued that some care must be taken in assigning a diffusion coefficient, a point that can be illustrated with a simple example. For a tightly bound ion-shell system, one in which no exchanges can take place between first and second solvation shells, it is obvious that the diffusion coefficient of first shell molecules must be identical to that of the ion (as the complex diffuses as a unit). Contrary to this expectation, this equality is not found in computer simulations for cases where it is manifest that no exchanges have taken place during the calculation. Figure 1(b) displays results obtained for  $\text{Mg}^{2+}$  in water (see below for computational details), a representative case for which the previous considerations apply. A linear regime is (apparently) attained after  $\approx 1$  ps for the mean square displacement (MSD) of the ion, for first solvation shell molecules, and for bulk solvent. The slope of the ion's MSD is clearly the smallest one, so that the conclusion that first shell molecules have a larger diffusion coefficient, but still smaller than that of bulk solvent, seems inescapable (the same conclusion is reached from analysis of the corresponding velocity autocorrelation functions, VACF). The computational origin of this artifact, together with the physical interpretation of the apparent faster diffusion of solvation molecules, will

be studied here in detail. Moreover, the implications for the estimation of the mean diffusion coefficient in different scenarios will also be addressed.

The paper is organized as follows: the basic formulas are derived in the following section, results for a couple of illustrative examples are described in Sec. III, and the final section is devoted to sketch a general picture and to summarize the main conclusions.

### II. THEORY

The rather simple explanation is that too short a cutoff is used for the MSD or VACF of the solvation shell molecules. Although, strictly speaking, the diffusion coefficient is a long

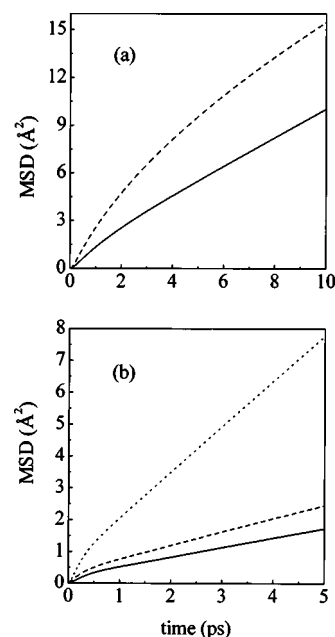


FIG. 1. Short time behavior of the mean square displacement for the systems studied. (a) Carbon (solid line) and chlorine (dashed line) atoms in  $\text{CCl}_4$ . (b)  $\text{Mg}^{2+}$  (solid line), first shell molecules (dashed line), and bulk water (dotted line).

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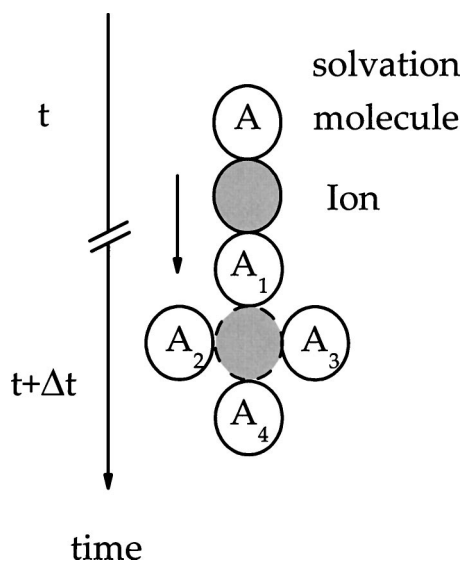


FIG. 2. Sketch of possible configurations after the ion and a first solvation shell molecule diffuse for a given time: a molecule initially located in position A can move to any of the sites  $A_i$ .

time property, it is usually determined with rather short simulations, to the point that within the time span usually taken for the MSD ( $\approx 5\text{--}10$  ps) the ion only diffuses by roughly one ionic diameter. If we take, for instance, a diffusion coefficient of  $\approx 1$  ( $10^{-9}$  m<sup>2</sup>/s), the square root of the corresponding MSD after 10 ps is  $\approx 2.5$  Å, i.e., of the order of the ionic diameter (a much shorter distance is obtained if computing the diffusion coefficient from the VACF). Although, remarkably, this suffices to produce an accurate diffusion coefficient for the ion, it will be shown within that this is not so for solvation shell molecules. The physical process that explains the apparently higher diffusion of the latter is easily understood from the sketch in Fig. 2 where, for the sake of clarity, the ion diffuses two diameters from its original position. During that time, a given solvation molecule A will travel the same distance as the ion (ending in position  $A_1$ ) only if it follows the ion rigidly. However, the motion of solvation molecules is a combination of translation and rotation around the ion, so that the molecule is also likely to end up in positions  $A_2$ ,  $A_3$ , or  $A_4$ , which imply a net displacement larger than that of the ion. If the MSD is averaged over all these possible outcomes an apparently higher diffusion of solvation molecules will be found. Obviously no such effect would be present if the ion would be allowed to diffuse by a large enough distance before computing the MSD, as the effect of rotations in random directions would cancel out.

These considerations can be readily translated into mathematical form. The position vector of a solvation molecule  $\vec{r}_M$  can be expressed in terms of that of the ion  $\vec{r}_I$  and the relative vector  $\vec{r}$

$$\vec{r}_M = \vec{r}_I + \vec{r}. \quad (1)$$

The MSD of the molecule

$$\Delta_M(t) = \langle [\vec{r}_M(t) - \vec{r}_M(0)]^2 \rangle \quad (2)$$

can thus be written in terms of the ion position and the relative vector as

$$\begin{aligned} \Delta_M(t) = & \Delta_I(t) + \langle [\vec{r}(t) - \vec{r}(0)]^2 \rangle \\ & + 2\langle [\vec{r}_I(t) - \vec{r}_I(0)] \cdot [\vec{r}(t) - \vec{r}(0)] \rangle. \end{aligned} \quad (3)$$

The last term is zero since there is no correlation on average between the ion position and the molecule-ion relative vector, so that one gets

$$\Delta_M(t) = \Delta_I(t) + \langle [\vec{r}(t) - \vec{r}(0)]^2 \rangle, \quad (4)$$

which can be rewritten as

$$\Delta_M(t) = \Delta_I(t) + 2[\bar{r}^2 - \langle \vec{r}(t) \cdot \vec{r}(0) \rangle], \quad (5)$$

where  $\bar{r}$  denotes the mean distance between the ion and the solvating molecule.

At long times the time correlation function contained into the last term will tend to zero so that the ion and solvation molecule mean square displacements  $[\Delta_I(t), \Delta_M(t)]$  will only differ by a constant value  $2\bar{r}^2$ . Therefore, since the diffusion coefficient is obtained as

$$D = \frac{1}{6} \lim_{t \rightarrow \infty} \frac{d[\Delta(t)]}{dt}, \quad (6)$$

the corresponding diffusion coefficients will be identical as expected. Of course, this is only strictly valid under the assumption of no exchanges between first and second shells, the limit in which  $\bar{r}$  is well defined.

To a very good approximation formula (5) can be written in a form that highlights the role of solvation shell rotation. For tight solvation shells the ion-molecule distance is almost constant, as reflected, for instance, in the steep first peak of the corresponding radial distribution function. Assuming a constant separation equal to the mean value, the relative vector can be written as  $\vec{r} \cong \bar{r}\hat{r}$  (where  $\hat{r}$  denotes the unit vector). From this approximation it follows:

$$\begin{aligned} \Delta_M(t) \cong & \Delta_I(t) + 2\bar{r}^2[1 - \langle \hat{r}(t) \cdot \hat{r}(0) \rangle] \\ = & \Delta_I(t) + 2\bar{r}^2[1 - P_1(t)], \end{aligned} \quad (7)$$

where  $P_1(t)$  stands for the Legendre polynomial which appears in the theory of rotational absorption spectroscopy,<sup>17</sup> and which after very short times is characterized by an almost exponential decay<sup>18</sup> [ $P_1(t) = e^{-t/\tau_1}$ ].  $\Delta_M(t)$  will only get parallel to  $\Delta_I(t)$  after  $P_1(t)$  has decayed to zero. As the rotation of a solvation complex made of several molecules will be slow,  $\tau_1$  can be longer than the time it takes the ion to reach diffusive behavior, this is why a MSD shorter than 10 ps is not capable of displaying the same diffusion coefficient for the ion and for the solvation shell molecules. Thus, Eq. (7) summarizes the basic idea of this work: at short times the mean square displacement of first solvation shell molecules ( $\Delta_M$ ) results from ion translation ( $\Delta_I$ ) plus rotation around the ion [embodied in the term containing  $P_1(t)$ ], while at longer times, after rotational correlation is lost, both MSD differ by just a constant and yield the same diffusion coefficient. It is interesting to note that the present image, according to which the ions with their solvation shells should be regarded as rigid spheres on a picosecond time scale, is in line with the conclusions reached from recent measures of rotational relaxation within the solvation shell.<sup>19</sup>

From Eq. (7) it is possible to get a pretty good idea of the time length required in order to obtain the expected identical values for the ion and solvation molecules diffusion coefficients. An estimate for the reorientational time can be derived from the rotational version of the Stokes–Einstein relation,<sup>20</sup> here applied to the ion plus first solvation shell complex

$$\tau = \frac{8\pi\eta R^3}{k_B T}, \quad (8)$$

where  $\eta$  stands for the bulk solvent viscosity and  $R$  for the radius of the complex. The time obtained for  $\text{Mg}^{2+}$  in water falls in the vicinity of 70 ps (see Sec. III B for details). The important point is that this time is more than one order of magnitude larger than the 5 ps used in Fig. 1(b).

Equation (7) also makes it clear why one can be misled by the shape of the MSD at such short times and assume that diffusive behavior has already been attained and a diffusion coefficient can be fitted. As previously stated, at intermediate times (shorter than  $\approx 10$  ps) the ion will have attained diffusive translation [so that its MSD will be linear in time:  $\Delta_I(t) = 6D_I t$ , where  $D_I$  denotes the ion's diffusion coefficient], but  $P_1(t)$  can still be approximated by its short time expansion [ $P_1(t) = 1 - (t/\tau_1) + \dots$ ]. If both expressions are inserted into Eq. (7) we get

$$\Delta_M(t) \approx 6D_I t + 2\bar{r}^2 \frac{t}{\tau_1} = \left( 6D_I + \frac{2\bar{r}^2}{\tau_1} \right) t, \quad (9)$$

i.e., a linear behavior is obtained, which mimics the characteristic diffusive behavior. From the latter expression one would estimate the solvation molecule diffusion coefficient as

$$D_M = D_I + \frac{\bar{r}^2}{3\tau_1}, \quad (10)$$

which in all cases exceeds the true value by a constant value  $\bar{r}^2/3\tau_1$ . Since  $\bar{r}^2$  is close to the shortest distance that can be attained and  $\tau_1$  is a rather long time, the overestimation is usually not substantial [as can be inferred for instance from Fig. 1(b)], but is noticeable enough to suggest that solvation molecules diffuse faster than the ion.

### III. NUMERICAL RESULTS

In this section a couple of illustrative examples will be described, both studied by means of molecular dynamics simulations. In all cases a time step of 1 fs was used and the temperature was kept constant by applying a Berendsen thermostat with a coupling constant of 10 ps.<sup>21</sup> Molecules were kept rigid using the SHAKE algorithm.<sup>22</sup> Further details for each system are given in the next sections.

#### A. Carbon tetrachloride

Liquid  $\text{CCl}_4$  will be used as a toy model: the C center will play the role of the ion and the Cl centers that of the solvation molecules. In this way one can eliminate several sources of statistical noise in order to check unambiguously the formulas developed above. For ion diffusion it takes a

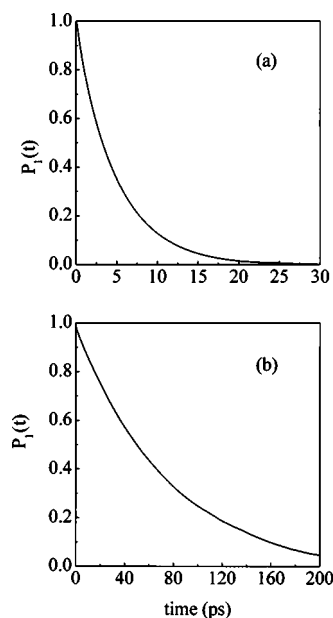


FIG. 3.  $P_1(t)$  for (a) chlorine atoms in  $\text{CCl}_4$  and (b) water molecules around  $\text{Mg}^{2+}$ .

long simulation time to get enough statistics as there is only one ion surrounded by several hundred solvent molecules, while in neat  $\text{CCl}_4$  statistics can be collected for every molecule. In addition, the approximation used to obtain formula (7), namely, that the ion–molecule distance is constant, here is exact. Finally, the rotation time for the molecule is known to be shorter than 10 ps,<sup>23</sup> so that no extremely long simulations are required. Molecular dynamics simulations of 1.5 ns were done for a system of 215 molecules. The reference temperature and density were, respectively, 298.15 K and  $1.579 \text{ g cm}^{-3}$ . The geometric and interaction parameters for carbon tetrachloride are given in Ref. 23. Figure 1(a) displays the MSD for carbon and for chlorine up to 10 ps. They both attain, to a good approximation, a linear behavior with different slopes within that time window. As in the case of  $\text{Mg}^{2+}$  in water [Fig. 1(b)] it is tempting to conclude that the chlorine centers have a larger diffusion coefficient than the carbon, which is obviously impossible for a rigid molecule. In order to analyze this case, formula (7) applies exactly, as the distances are fixed. The rotational correlation function  $P_1(t)$  is displayed in Fig. 3(a), it is well represented by an exponential decay with  $\tau_1 = 4.8$  ps, so that it is safe to consider it has vanished after  $\approx 20$ – $30$  ps for practical purposes. Therefore, according to Eq. (7), after that time the MSD for the C center and that for the Cl centers should be parallel and differ by a constant amount of  $2\bar{r}^2$  (which in this case, with a C–Cl bond of  $1.766 \text{ \AA}$ , is equal to  $6.24 \text{ \AA}^2$ ). The results from the simulation are in perfect quantitative agreement with this expected behavior, as displayed in Fig. 4(a).

#### B. $\text{Mg}^{2+}$ in liquid water

For this system the lifetime of a molecule within the first solvation shell (estimated to fall in the microsecond range<sup>24</sup>) is much longer than the time required for the rotational relaxation of the first shell solvation complex (estimated in Sec. II to be lower than 100 ps). Therefore, the formulas

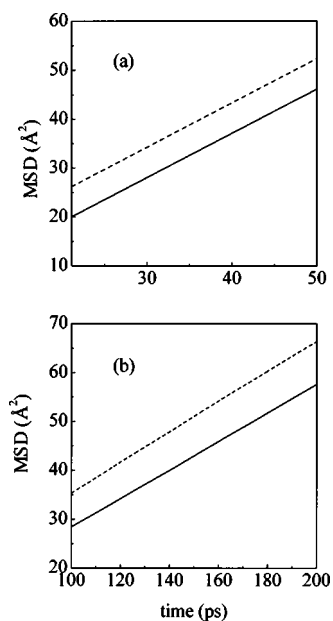


FIG. 4. Long time behavior of the mean square displacement for the systems studied. (a) Carbon (solid line) and chlorine (dashed line) atoms in  $\text{CCl}_4$ . (b)  $\text{Mg}^{2+}$  (solid line) and first shell molecules (dashed line).

developed in Sec. II for tightly bound complexes should be valid. Simulations of 15.0 ns were done for a system of 215 SPC/E water molecules<sup>25</sup> and one magnesium ion. The reference temperature and density were set, respectively, to 298.15 K and  $0.997 \text{ g cm}^{-3}$ . The Lennard-Jones interaction parameters for  $\text{Mg}^{2+}$ -water were taken from Ref. 26. With these parameters the first solvation shell contains six molecules, and none of them is observed to leave the first shell during the course of the simulation.

As previously stated, the estimated rotational relaxation time can be rather long. The theoretical prediction is only approximate since, besides the phenomenological character of Eq. (8) on which it relies, water viscosity  $\eta$ , for the SPC/E model used here, is estimated<sup>27,28</sup> to fall in the range 0.71–0.91 [which brackets the experimental value of 0.85 cP (Ref. 29)]. Regarding the radius of the complex, we have taken 2.41 Å, the distance at which first solvation shell population has decayed to zero, as estimated from the ion-oxygen radial distribution function, which is consistent with the results from a variety of (polarizable and nonpolarizable) models.<sup>27,30,31</sup> The rotational time thus obtained applying Eq. (8) is 68–87 ps (depending on the value of the viscosity). This theoretical estimation is confirmed to a large extent in Fig. 3(b), which displays the computed  $P_1(t)$ . An exponential fit results in a time of  $\tau_1=78$  ps so that even for a time as long as 200 ps this function will have a non-negligible contribution. This implies, according to the considerations in Sec. II, that in order to get a diffusion coefficient for solvation shell molecules equal to that of the ion, the corresponding MSD should be several hundred picoseconds long, what is in stark contrast with the 5–10 ps range usually chosen. Figure 4(b) shows that for times larger than 100 ps both MSD are parallel to a good approximation and differ by a constant value which approaches (see below) the theoretical prediction  $2\bar{r}^2=9.24 \text{ Å}^2$ , where we have taken  $\bar{r}=2.15 \text{ Å}$  (the

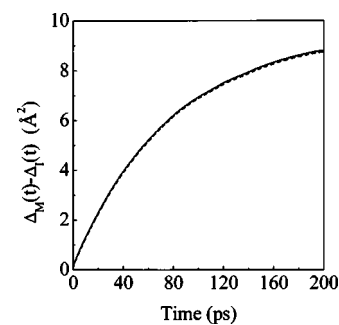


FIG. 5. Dashed line: difference between ion and solvation molecules mean square displacements. Solid line: approximate result predicted by Eq. (7)  $\{2\bar{r}^2[1-P_1(t)]\}$ .

position of the first maximum of the radial distribution function). The accord is excellent considering that in this case the ion-molecule distance is only approximately constant. The rather small disagreement is more visible in Fig. 5, where the function  $2\bar{r}^2[1-P_1(t)]$  is compared with the difference  $\Delta_M(t) - \Delta_I(t)$ . According to Eq. (7) both functions are only approximately equal, although from Fig. 5 it is clear that the deviation is negligible in this case, particularly considering that the statistics obtained from a single ion simulation can be subject to some noise at such long times. It can also be easily appreciated in Fig. 5 how  $\Delta_M(t) - \Delta_I(t)$  asymptotically approaches the theoretical value ( $9.24 \text{ Å}^2$ ).

## IV. DISCUSSION

The role played by exchanges between first and second solvation shells remains to be addressed. The corresponding time scale is critically dependent on the system under study: for monoatomic ions dissolved in water it spans 18 orders of magnitude,<sup>24</sup> with the lower limit estimated to fall within the picosecond range and the upper limit reaching up to Ms. The very long times involved in most cases constitute a barrier for computational studies, it is only recently that the dynamics and kinetics of this process have started to be addressed<sup>32–36</sup> using numerical methods borrowed from reaction rate theory. The bottom line of the previous sections is that, as long as the exchange time scale is much longer than that for rotational relaxation, the diffusion coefficient of first solvation shell molecules should be taken equal to that of the ion. Indeed, the case of  $\text{Mg}^{2+}$  is probably representative of the majority of cases for multiply charged monoatomic ions in water:<sup>24</sup> the rotational relaxation time will be of the order of 0.1 ns and the exchange time higher than 1 ns. Overestimations of the diffusion coefficient [close to the value given in Eq. (10)] will be obtained if short MSD (of the order of 0.01 ns) are used, and are due to the transient rotational relaxation of the complex at short times. The situation is less well defined for singly charged ions in water, while for other liquids and/or ions the field is largely unexplored.

In order to get a general view that includes systems for which the time scales are not so clear cut it is important to note that, indeed, any diffusion coefficient for first shell molecules ( $D_{\text{first}}$ ) is a temporary one since, eventually, exchanges will occur and the molecule will diffuse as bulk solvent. This formulation makes it clear that the value taken for ( $D_{\text{first}}$ ) is

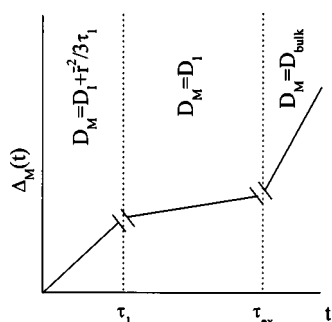


FIG. 6. Sketch of the typical expected behavior for the MSD of molecules initially belonging to the first solvation shell. The case shown here corresponds to a tightly bound shell as  $\tau_{\text{ex}} \gg \tau_1$ .

actually a matter of definition, which will only be valid for times lower than  $\tau_{\text{ex}}$ . In other words,  $\Delta_M(t)$  (a function that results from an average over all molecules initially belonging to the first solvation shell) will go through different (linear) regimes, each one characterized by a temporary diffusion coefficient. This expected behavior is sketched in Fig. 6 for a tightly bound solvation shell: a fit of the MSD for times lower than  $\tau_1$  would result in the value given in Eq. (10), for times in the range  $\tau_1 < t < \tau_{\text{ex}}$  the fit would yield  $D_M = D_I$ , and, finally, for times larger than  $\tau_{\text{ex}}$  it is clear that one would obtain  $D_M = D_{\text{bulk}}$ . This suggests that a sensible definition of the diffusion coefficient should be based on the ratio between the exchange time  $\tau_{\text{ex}}$  and the rotational relaxation time  $\tau_1$  for the system of interest. As previously stated, if  $\tau_{\text{ex}} \gg \tau_1$  it seems reasonable to define  $D_{\text{first}} \equiv D_{\text{ion}}$ , without requiring the actual calculation of the MSD. Indeed such calculation would not provide any new information and, in addition, it would involve extremely long simulations (as illustrated by the  $\text{Mg}^{2+}$  case). If  $\tau_{\text{ex}} \approx \tau_1$  (both falling within the same order of magnitude), i.e., if (on average) solvation molecules leave the first shell shortly after rotation of the complex has relaxed, then according to Eq. (10) it should probably be a reasonable choice to take  $D_{\text{first}} \equiv D_{\text{ion}} + \bar{r}^2/3\tau_1$ . To stress that this is in fact a definition one can note that it is not possible to obtain such result from simulation. If all solvation molecules would be used for the calculation, given that a fraction of them would escape during the simulation run, a mean between diffusion in the first shell and (the much faster) bulk diffusion would be obtained; on the contrary, if one would try to compute  $D_{\text{first}}$  only using those solvation molecules that do not escape, the result would initially be equal to Eq. (10) and subsequently be followed by a value equal to  $D_{\text{ion}}$ . Finally, if  $\tau_{\text{ex}} \leq \tau_1$ , i.e., most of the molecules are exchanged before the complex can rotate significantly, it does not seem possible to talk of a  $D_{\text{first}}$  clearly different from that of bulk solvent molecules. To summarize, simple definitions for  $D_{\text{first}}$  seem possible which take into account the role of exchanges. The computer simulations required to estimate the diffusion coefficient are not direct calculations of the MSD for solva-

tion shell molecules (which have been argued to be problematic in all cases), but rather the solvation shell lifetime and rotational relaxation time of the complex.

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