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### Title

Isotopic mass-dependence of noble gas diffusion coefficients in water

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### Authors

Bourg, I.C.  
Sposito, G.

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**Isotopic fractionation of noble gases by diffusion in liquid water. 1. Molecular dynamics simulations**

Ian C. Bourg\* and Garrison Sposito

Geochemistry Department, Earth Sciences Division, Lawrence Berkeley National Laboratory,  
Berkeley, CA 94720, USA

\*Author to whom correspondence should be addressed ([ibourg@nature.berkeley.edu](mailto:ibourg@nature.berkeley.edu))

## Abstract

Despite their great importance in low-temperature geochemistry, self-diffusion coefficients of noble gas isotopes in liquid water ( $D$ ) have been measured only for the major isotopes of helium, neon, krypton and xenon. Data on the self-diffusion coefficients of minor noble gas isotopes are essentially non-existent and typically are estimated by a kinetic theory model in which  $D$  varies as the inverse square root of the isotopic mass ( $m$ ):  $D \propto m^{-0.5}$ . To examine the validity of the kinetic theory model, we performed molecular dynamics (MD) simulations of the diffusion of noble gases in ambient liquid water with an accurate set of noble gas-water interaction potentials. Our simulation results agree with available experimental data on the solvation structure and self-diffusion coefficients of the major noble gas isotopes in liquid water and reveal for the first time that the isotopic mass-dependence of all noble gas self-diffusion coefficients has the power-law form  $D \propto m^{-\beta}$  with  $0 < \beta < 0.2$ . Thus our results call into serious question the widespread assumption that the ‘square root’ model can be applied to estimate the kinetic fractionation of noble gas isotopes caused by diffusion in ambient liquid water.

## INTRODUCTION

Dissolved noble gases have emerged as important geochemical indicators of transport and paleoclimate in hydrological basins (Stute et al., 1995; Castro et al., 1998, 2007; Aeschbach-Hertig et al., 1999; Peeters et al., 2003; Price et al., 2003; Hall et al., 2005; Zhou et al., 2005; LaBolle et al., 2006; Ingram et al., 2007), lacustrine sediments (Kipfer et al., 2002; Poreda et al., 2004; Strassmann et al., 2005; Brennwald et al., 2005), aquitards (Rübel et al., 2002; Hendry et al., 2005; Osenbrück et al., 2005), engineered clay barriers (Higashihara et al., 2005) and the oceans (Rodehacke et al., 2007). Brennwald et al. (2005) used Ne, Ar, Kr and Xe concentrations and  $^{20}\text{Ne}/^{22}\text{Ne}$  and  $^{36}\text{Ar}/^{40}\text{Ar}$  isotopic ratios to estimate rates of methane release from anoxic lake sediments. Rübel et al. (2002) used  $^4\text{He}$  concentrations and  $^{40}\text{Ar}/^{36}\text{Ar}$  isotopic ratios to evaluate the relative importance of advective and diffusive transport in a clay-rich geological formation proposed to become host to a Swiss high-level radioactive waste repository. Stute et al. (1995) used Ne, Ar, Kr and Xe concentrations in a Brazilian aquifer to reconstruct continental temperatures during the last 30,000 years. In the paleotemperature reconstruction method of Stute et al. (1995), noble gas concentrations in aquifer water were assumed to result from three successive steps: equilibrium dissolution of noble gases at the phreatic surface at the time of groundwater recharge, uptake of excess noble gas through complete dissolution of trapped atmospheric air near the water table, and diffusion-controlled release of a fraction of the excess noble gas (Stute et al., 1995; Aeschbach-Hertig et al., 1999; Kipfer et al., 2002). For each noble gas other than Ne, the mass fraction released during the third step ( $1-f_{NG}$ ) is related to the mass fraction of neon released during the third step ( $1-f_{\text{Ne}}$ ) by the well-known Rayleigh fractionation formula (if  $D_{NG}$  is the diffusion coefficient of a noble gas in water):

$$f_{NG} = f_{\text{Ne}}^{D_{NG}/D_{\text{Ne}}} \quad (1)$$

24 Pore water concentrations of the four noble gases Ne, Ar, Kr and Xe then allow the calculation  
25 of four unknown parameters: ground temperature and atmospheric pressure at the time and  
26 location of groundwater recharge, total amount of dissolved ‘excess air’, and  $f_{\text{Ne}}$  (Stute et al.,  
27 1995; Aeschbach-Hertig et al., 1999). Paleotemperatures calculated in this way are the most  
28 sensitive to Xe concentrations and diffusion coefficients, because the temperature dependence of  
29 noble gas solubility increases with atomic mass (Aeschbach-Hertig et al., 1999).

30 Despite this importance of noble gas diffusion coefficients in low-temperature geochemistry,  
31 remarkably few measurements of these critical parameters have been reported. Jähne et al.  
32 (1987) have provided perhaps the most precise measurements of diffusion coefficients of noble  
33 gases in liquid water at 298 K (Table 1). Pulsed-field-gradient nuclear magnetic resonance (PFG-  
34 NMR) studies (Weingärtner et al., 1992; Holz et al., 1994) confirmed the result of Jähne et al.  
35 (1987) for Ne diffusion, but yielded a significantly larger Xe diffusion coefficient (Weingärtner  
36 et al., 1992). No other experimental data on noble gas diffusion in liquid water appear to have  
37 been published during the last twenty years. Data on the diffusion coefficients of minor noble gas  
38 isotopes are very scarce; they consist of a single measurement of the ratio of the diffusion  
39 coefficients of  $^3\text{He}$  and  $^4\text{He}$ :  $D(^3\text{He})/D(^4\text{He}) = 1.15 \pm 0.03$  (Jähne et al., 1987).

40 With this paucity of experimental data, most geochemical studies of noble gas solutes have  
41 relied upon the He, Ne, Kr and Xe diffusion coefficients measured by Jähne et al. (1987)  
42 together with an  $^{40}\text{Ar}$  diffusion coefficient estimated by extrapolation of their results (Stute et al.,  
43 1995; Osenbrück et al., 1998; Aeschbach-Hertig et al., 1999; Ballentine et al., 2002; Kipfer et al.,  
44 2002; Rübel et al., 2002; Holocher et al., 2003; Peeters et al., 2003; Price et al., 2003; Poreda et  
45 al., 2004; Brennwald et al., 2005; Hendry et al., 2005; Strassmann et al., 2005; Zhou et al., 2005;  
46 Hall et al., 2006; Ingram et al., 2007; Klump et al., 2007; Rodehacke et al., 2007). Diffusion

47 coefficients of minor noble gas isotopes in liquid water for which no data exist then have  
48 routinely been estimated using the kinetic-theory model  $D \propto 1/\mu^{0.5}$  [ $\mu$  is the solvent-solute  
49 reduced mass,  $\mu = mm_0/(m + m_0)$ , if  $m$  and  $m_0$  are solute and solvent molecular masses (LaBolle  
50 et al., 2006)] or, more commonly, using the ‘square root’ relation  $D \propto 1/m^{0.5}$ , which is obtained  
51 from the kinetic-theory model under the assumption that the hydrogen-bonded water network  
52 behaves as an ‘effective particle’ of infinitely large mass ( $m_0 \gg m$ ) (Ballentine et al., 2002;  
53 Lippmann et al., 2003; Peeters et al., 2003; Brennwald et al., 2005; Strassmann et al., 2005; Zhou  
54 et al., 2005; Hall et al., 2006; Klump et al., 2007). The ‘square root’ model, which apparently has  
55 never been tested directly, either experimentally or theoretically, in conjunction with measured  
56  $^{20}\text{Ne}/^{22}\text{Ne}$  or  $^{36}\text{Ar}/^{40}\text{Ar}$  isotope ratios has led to widespread dismissal of diffusion in pore water as  
57 a significant contributor to noble gas transport or excess noble gas uptake in subsurface water  
58 (Kipfer et al., 2002; Peeters et al., 2003; Brennwald et al., 2005; Zhou et al., 2005; Hall et al.,  
59 2006; Klump et al., 2006, 2007).

60 Very recently Richter et al. (2006) demonstrated that the diffusion coefficients of ionic  
61 solutes in liquid water do not follow the ‘square-root’ model in their dependence on isotopic  
62 mass. They provided the first precise measurements of the kinetic fractionation of Mg, Li, and Cl  
63 isotopes by diffusion in liquid water and showed that a more general inverse power-law relation,  
64  $D \propto m^{-\beta}$ , was applicable, with  $\beta_{\text{Mg}} \approx 0$ ,  $\beta_{\text{Li}} = 0.0148 \pm 0.0017$  and  $\beta_{\text{Cl}} = 0.026 \pm 0.014$ . Subsequent  
65 molecular dynamics (MD) simulations of the self-diffusion of these ions in liquid water (Bourg  
66 and Sposito, 2007) fully corroborated the small experimental  $\beta$ -values and provided insight  
67 based on hydration shell dynamics as to why  $\beta$  differed among the three ions.

68 Very low solubility in ambient water currently prevents use of the method of Richter et al.  
69 (2006) to measure the mass-dependence of noble gas diffusion coefficients. However, these

70 diffusion coefficients can be calculated for both major and minor isotopes by accurate MD  
71 simulation. The accuracy of simulations performed for this purpose is limited mainly by the  
72 quality of the water-water and noble gas-water intermolecular potentials used. Previous  
73 molecular simulations of noble gas solute behavior in ambient water (Swope and Andersen,  
74 1984; Straatsma et al., 1986; Tanaka and Nakanishi, 1991; Guillot et al., 1991; Lazaridis and  
75 Paulaitis, 1994; Lau and Gerig, 1995; Arthur and Haymet, 1998; Ohmori and Kimura, 2005)  
76 have incorporated gas-water potentials calculated either from outdated gas-gas interaction data  
77 (Hirschfelder et al., 1954) or with inaccurate (Lorentz-Berthelot) combining rules. Moreover, the  
78 noble gas-water potentials used in these studies were tested only by comparing model predictions  
79 with experimental data on the enthalpy and Gibbs energy of hydration. Gibbs energies of noble  
80 gas hydration in ambient water were predicted with an inaccuracy ( $\approx 4 \text{ kJ mol}^{-1}$ ) similar to the  
81 difference between the Gibbs energies of solvation of Ne and Xe (Arthur and Haymet, 1998).  
82 Simulated noble gas diffusion coefficients (Ohmori and Kimura, 2005) in fact overestimated  
83 most experimental data by 15-40 % (Table 1).

84 In the present study, MD simulations of noble gas diffusion in liquid water were carried out  
85 with a new set of gas-water potentials calculated with gas-gas interaction data (Aziz, 1984; Tang  
86 and Toennies, 1986) that are more recent than those of Hirschfelder et al. (1954) and with  
87 combining rules that are more accurate than the Lorentz-Berthelot rules (Kong, 1973). Our  
88 results corroborate available data on the solvation structure and diffusion coefficients of noble  
89 gases in liquid water while providing the first direct determination of the isotopic mass-  
90 dependence of the diffusion coefficients.

91

## SIMULATION METHODS

92  
93 Molecular dynamics simulations (8 ns interval, preceded by 202 ps of equilibration at 298 K)  
94 were carried out with the program MOLLY 3.6 (Refson, 2000) for one noble gas atom and 550  
95 water molecules in a periodically replicated, cubic cell (microcanonical ensemble, 0.997 kg dm<sup>-3</sup>  
96 density) using the methodology of Bourg and Sposito (2007). Molecular trajectories were  
97 calculated by solving the Newton-Euler equations (with a 1 fs time step) with a form of the  
98 Beeman algorithm, the most accurate of all “Verlet-equivalent” algorithms (Refson, 2000).  
99 Long-range interactions were treated by Ewald summation with parameters chosen to yield an  
100 Ewald sum accuracy of 99.99%. Total energy drift during each 8 ns simulation was about 0.002  
101 %. Liquid water was described with the extended simple point charge (SPC/E) model of  
102 Berendsen et al. (1987). Despite its simplicity [fixed O-H bond lengths (1 Å), H-O-H angle  
103 (109.47°) and atomic charges ( $q_O = -0.8476 e$  and  $q_H = 0.4238 e$ )] the SPC/E model predicts the  
104 self-diffusion coefficient of water at 298 K to within 4 % (Smith and Dang, 1994), the static  
105 dielectric constant of water at 324.2 and 523 K (at 1 kg dm<sup>-3</sup> density) to within 2 and 4 %  
106 (Wasserman et al., 1995), and the X-ray scattering intensities of liquid water at 298 and 350 K to  
107 within 1.8 % (Hura et al., 2003).

108 On the SPC/E model, short-range non-Coulombic interactions ( $\phi_{ij}$ , kJ mol<sup>-1</sup>) between water O  
109 atoms are described with the Lennard-Jones (LJ) 6-12 model:

$$110 \quad \phi_{ij}(r_{ij}) = 4 \epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} \right] \quad (2)$$

111 where  $r_{ij}$  (Å) is the interatomic distance and  $2^{1/6}\sigma_{ij}$  and  $\epsilon_{ij}$  are the location (Å) and depth of the  
112 potential well (J mol<sup>-1</sup>). The LJ 6-12 model, with noble gas  $\sigma_{ii}$  and  $\epsilon_{ii}$  parameters compiled by  
113 Aziz (1984), accurately describes interactions between noble gas atoms in the region of the



114 potential well (Tang and Toennies, 1986). In the present study,  $\sigma_{ij}$  and  $\epsilon_{ij}$  parameters for the  
 115 interaction between noble gases and water O atoms were calculated from noble gas and SPC/E  
 116 water  $\sigma_{ii}$  and  $\epsilon_{ii}$  parameters with the combining rules of Kong (1973):

$$117 \quad \epsilon_{ij} \sigma_{ij}^6 = \sqrt{\epsilon_{ii} \sigma_{ii}^6 \cdot \epsilon_{jj} \sigma_{jj}^6} \quad (3a)$$

$$118 \quad \epsilon_{ij} \sigma_{ij}^{12} = \left[ \frac{(\epsilon_{ii} \sigma_{ii}^{12})^{1/13} + (\epsilon_{jj} \sigma_{jj}^{12})^{1/13}}{2} \right]^{13} \quad (3b)$$

119 Equations 3a,b, combined with the kinetic theory of gases, predict diffusion coefficients in  
 120 binary mixtures of most noble gases with less than 2 % inaccuracy over a broad temperature  
 121 range (300 to 1400 K) (Kong, 1973). The same diffusion data, however, are poorly predicted if  
 122  $\sigma_{ij}$  and  $\epsilon_{ij}$  are calculated with the Lorentz-Berthelot rules (Hogervorst, 1971). The Lennard-Jones  
 123 parameters used in the present study are compiled in Table 2.

124 Simulations were carried out for  $^4\text{He}$ ,  $^{20}\text{Ne}$ ,  $^{40}\text{Ar}$ ,  $^{84}\text{Kr}$  and  $^{132}\text{Xe}$  in liquid water to test the  
 125 quality of the noble gas-water interaction potentials in Table 2 and for a range of hypothetical  
 126 isotopes of He, Ne, Ar and Xe ( $m = 4\text{-}132$  Da) to determine the isotopic mass dependence of  
 127 solute self-diffusion coefficients, following the methodology of Bourg and Sposito (2007).  
 128 Previous studies have used MD simulation with a broad range of solute mass to infer solute  
 129 isotopic effects, mainly in Lennard-Jones or hard-sphere fluids (Alder et al., 1974; Nuevo et al.,  
 130 1995; Willeke, 2003) but also in liquid water (Wilson et al., 1985; Møller et al., 2005; Bourg and  
 131 Sposito, 2007). Radial distribution functions of O and H atoms near noble gas (NG) solutes and  
 132 noble gas velocity autocorrelation functions ( $\langle \mathbf{v}(0) \cdot \mathbf{v}(t) \rangle$ ) were calculated with standard methods  
 133 (Allen and Tildesley, 1987; Refson, 2000). The average number of oxygen atoms in the first  
 134 solvation shell of each noble gas ( $n^0$ ) was calculated by integrating the function  $4\pi r^2 g_{NGO}(r)$  to its

135 first minimum ( $r_{\min}$ ). Solute self-diffusion coefficients were calculated with the well-known  
136 Green-Kubo relation (Allen and Tildesley, 1987):

$$137 \quad D = \frac{1}{3} \lim_{\tau \rightarrow \infty} \int_0^{\tau} \langle \mathbf{v}(0) \cdot \mathbf{v}(t) \rangle dt \quad (4)$$

138 The ‘infinite limit’ in equation 4 was approximated accurately by taking the average of  $D$ -values  
139 obtained for  $\tau = 2.4$  to  $2.5$  ps.

140

### 141 SOLVATION STRUCTURE

142 The solvation structure near  $^4\text{He}$ ,  $^{20}\text{Ne}$ ,  $^{40}\text{Ar}$ ,  $^{84}\text{Kr}$  and  $^{132}\text{Xe}$  in ambient liquid water as  
143 revealed by radial distribution functions is summarized in Figure 1 [radial distribution functions  
144 for O and H atoms near noble gas solutes,  $g_{\text{NGO}}(r)$  and  $g_{\text{NGH}}(r)$ ] and Table 3 [location of the first  
145 maximum ( $r_{\max}$ ) and minimum ( $r_{\min}$ ) of each  $g_{\text{NGO}}(r)$  function and average number of water  
146 molecules in the first solvation shell ( $n^0$ )]. The slightly shorter first-shell peak distance for  
147  $g_{\text{NGH}}(r)$  as compared to  $g_{\text{NGO}}(r)$  indicates that first-shell water molecules are preferentially  
148 oriented in a “straddling” configuration (Figure 2), such that one of the apices of the water  
149 tetrahedron points away from the noble gas atom (Geiger et al., 1979; Rapaport and Scheraga,  
150 1982). This preferred configuration, however, does not require the existence of a static clathrate  
151 cage: it exists even for small hydrophobic solutes (H, He, Ne) that diffuse much more rapidly  
152 than do nearby water molecules and have a ‘floppy’ solvation shell (Kirchner et al., 2002).  
153 Radial distribution functions for the smallest noble gas atoms, He and Ne, (Figure 1) are similar  
154 to those obtained by Kirchner et al. (2002) by *ab initio* MD simulation of a solvated uncharged H  
155 atom. The evident absence of solvation structure beyond the first shell is consistent with previous  
156 MD simulation studies (Straatsma et al., 1986; Guillot et al., 1991).

157 No experimental data appear to be available concerning the solvation structure around noble  
 158 gases in ambient liquid water. Bowron et al. (1998) used extended X-ray absorption fine-  
 159 structure (EXAFS) spectroscopy to determine the radial distribution function of O atoms around  
 160 Kr in water at 20 bar and 277 to 348 K. If the results of Bowron et al. (1998) are extrapolated to  
 161 ambient pressure, based on the lack of pressure-dependence of Kr solvation structure in water  
 162 between 20 to 700 bar (Filipponi et al., 1997; Bowron et al., 2001), they are in good agreement  
 163 with our MD simulation results (Figure 3a). Broadbent and Neilson (1994) calculated the total  
 164 distribution function of argon [ $G_{Ar}(r)$ ] in D<sub>2</sub>O at 298 K and ~240 bar from isotopic-difference  
 165 neutron diffraction data on natural Ar (<sup>Nat</sup>Ar) and <sup>36</sup>Ar aqueous solutions. The total distribution  
 166 function is related to the partial radial distribution functions by:

$$167 \quad G_{Ar}(r) = A[g_{NGO}(r) - 1] + B[g_{NGH}(r) - 1] + C[g_{ArAr}(r) - 1] \quad (5)$$

168 where the weighting coefficients have the values  $A = 1.247$ ,  $B = 2.869$  and  $C \approx 0$  at 240 bar  
 169 (Broadbent and Neilson, 1994). Our MD simulation of  $G_{Ar}$  based on the partial radial distribution  
 170 functions is also consistent with the experimental  $G_{Ar}$  (Figure 3b).

171

## 172 **DIFFUSION COEFFICIENTS OF MAJOR NOBLE GAS ISOTOPES**

173 Experimental and simulation results on the diffusion coefficients of major noble gas isotopes  
 174 in water at 298 K are shown in Table 1. The self-diffusion coefficients predicted in the present  
 175 study are consistent with the experimental data of Jähne et al. (1987). Notably, our Xe simulation  
 176 results support the experimental results of Jähne et al. (1987), not those of Weingärtner et al.  
 177 (1992). The widespread method (Aeschbach-Hertig et al., 1999; Ballentine et al., 2002; Holocher  
 178 et al., 2003; Peeters et al., 2003; Brennwald et al., 2005; Strassmann et al., 2005; Zhou et al.,  
 179 2005; Ingram et al., 2007) of estimating Ar diffusion coefficients by extrapolation of the He, Ne,

180 Kr and Xe diffusion data of Jähne et al. (1987) yields  $D_{\text{Ar}}$  values consistent with our Ar  
181 simulation results [ $D_{\text{Ar}} = 2.69 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$  at 298 K (Holocher et al., 2003)].

182

### 183 **ISOTOPIC MASS DEPENDENCE OF NOBLE GAS DIFFUSION COEFFICIENTS**

184 The mass dependencies of the self-diffusion coefficients of noble gas isotopes as obtained by  
185 MD simulation (Table 4) were analyzed by plotting average  $\log D$  values obtained during four 2  
186 ns ‘blocks’ of each 8 ns simulation vs.  $\log m$ . Linear regression of the data shows that the  
187 isotopic mass-dependence of noble gas self-diffusion coefficients has the generic power-law  
188 form:

$$189 \quad D \propto m^{\beta} \quad (6)$$

190 with  $\beta > 0$ , as proposed originally for ionic solutes by Richter et al. (2006) (Linear regression of  
191 simulation results as  $\log D$  vs.  $\log \mu$  yielded a poorer fit than equation 6 for He, Ne, Ar and Xe).

192 The linear regression parameters obtained with equation 6 (Table 5) indicate that  $\beta < 0.2$ , in  
193 stunning contradiction with the ‘square root’ model currently used in noble gas geochemistry  
194 (Ballentine et al., 2002; Lippmann et al., 2003; Peeters et al., 2003; Brennwald et al., 2005;  
195 Strassmann et al., 2005; Zhou et al., 2005; Hall et al., 2006; Klump et al., 2006, 2007). Although  
196 quantum isotope effects may enhance the isotopic mass dependence of solute diffusion  
197 coefficients beyond that predicted by our classical MD simulations, these effects should be  
198 negligible for Ne, Ar and Xe, for which the characteristic length scale of solute/water  
199 interactions ( $r_{\text{max}}$ , Table 3) is more than 25 times the thermal de Broglie wavelength under  
200 ambient conditions [ $\Lambda = (h^2/2\pi mk_{\text{B}}T)^{1/2}$ , if  $h$  and  $k_{\text{B}}$  are the Planck and Boltzmann constants  
201 (Hansen and McDonald, 1986); for  $^3\text{He}$  and  $^4\text{He}$ , however,  $r_{\text{max}}/\Lambda \approx 5$  and 8].

202 'Brownian' particles (i.e., solutes that are much larger and heavier than the solvent  
203 molecules) diffuse according to the well-known Stokes-Einstein relation, which predicts that the  
204 self-diffusion coefficient should be independent of isotopic mass (i.e.,  $\beta = 0$  in equation 6). The  
205 decrease in  $\beta$ -values in the order  $\text{He} \geq \text{Ne} > \text{Ar} \geq \text{Xe}$  that we observed suggests that the larger  
206 noble gas solutes indeed behave in a more 'Brownian' manner than do the smaller noble gas  
207 solutes. If the solute radius  $r$  ( $\text{\AA}$ ) is estimated as  $r_{\text{max}}$  for  $g_{\text{NGO}}$  (Table 3) minus half of  $r_{\text{max}}$  for the  
208 O-O radial distribution function in pure water ( $1.4 \text{ \AA}$ ), then our  $\beta$ -values are well described by  
209 the power-law relation  $\beta = B (1/r)^\gamma$  with  $B = 0.55 \pm 0.17$  and  $\gamma = 2.49 \pm 0.45$  ( $R^2 = 0.98$ ).

210 Comparison of noble gas diffusion coefficients calculated with the Stokes-Einstein relation  
211 [ $D = k_B T / (C \pi \mu r)$ , where  $k_B$  is the Boltzmann constant,  $T$  is absolute temperature, and  $\mu$  is the  
212 shear viscosity of ambient water, with  $C = 4$  for 'slip' conditions at the solute-water boundary  
213 (Tyrrell and Harris, 1984)] or from MD simulations of 4 Da and 132 Da isotopes of He, Ne, Ar  
214 and Xe confirm the quasi-'Brownian' behavior of  $^{132}\text{Xe}$  in ambient liquid water (Figure 4). With  
215 decreasing solute mass or radius, however, the Stokes-Einstein relation increasingly  
216 underestimates noble gas diffusion coefficients in liquid water.

217

## 218 CONCLUSIONS

219 A new set of noble-gas water interaction parameters, derived with improved combining rules  
220 and noble gas-noble gas interaction parameters, allowed successful prediction of all available  
221 experimental data on the solvation structure and self-diffusion coefficients of major noble gas  
222 isotopes in ambient liquid water. In particular, our simulation results corroborate the self-  
223 diffusion coefficients of major noble gas isotopes measured by Jähne et al. (1987) that are widely  
224 used in geochemical studies (Stute et al., 1995; Osenbrück et al., 1998; Aeschbach-Hertig et al.,

225 1999; Ballentine et al., 2002; Rübél et al., 2002; Peeters et al., 2003; Price et al., 2003; Poreda et  
226 al., 2004; Brennwald et al., 2005; Hendry et al., 2005; Strassmann et al., 2005; Zhou et al., 2005;  
227 Klump et al., 2007; Rodehacke et al., 2007). Our MD simulations carried out with a broad range  
228 of solute isotopic masses revealed that noble gas self-diffusion coefficients in water follow an  
229 inverse power-law mass-dependence,  $D \propto m^\beta$ , with  $0 < \beta < 0.2$ . Thus, the commonly invoked  
230 ‘square root’ model of noble gas isotope fractionation by diffusion in liquid water (Ballentine et  
231 al., 2002; Lippmann et al., 2003; Peeters et al., 2003; Brennwald et al., 2005; Strassmann et al.,  
232 2005; Zhou et al., 2005; Hall et al., 2006; Klump et al., 2006, 2007) overestimates the strength of  
233 the mass-dependence of noble gas self-diffusion coefficients.

234

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Table 1. Self-diffusion coefficients ( $10^{-9} \text{ m}^2 \text{ s}^{-1}$ ) of noble gases in ambient liquid water.

Noble gas	Experimental (Jähne et al., 1987)	Experimental (Weingärtner et al., 1992; Holz et al., 1994)	MD simulation (Ohmori and Kimura, 2005)	MD simulation (this study)
He	$7.22 \pm 0.36$		$10.0 \pm 0.9$	$7.85 \pm 0.54$
Ne	$4.16 \pm 0.21$	$4.18 \pm 0.20$	$4.9 \pm 0.2$	$4.78 \pm 0.37$
Ar			$2.4 \pm 0.1$	$2.57 \pm 0.15$
Kr	$1.84 \pm 0.09$		$2.1 \pm 0.1$	$1.97 \pm 0.13$
Xe	$1.47 \pm 0.07$	$1.90 \pm 0.09^a$	$1.6 \pm 0.1$	$1.57 \pm 0.11$

<sup>a</sup> Confidence interval calculated with the assumption that NMR data for Ne and Xe diffusion have similar coefficients of variation.

Table 2. Lennard-Jones 6-12 potential parameters.

Atom pair	$\sigma$ (Å)	$\epsilon$ (kJ mol <sup>-1</sup> )
<i>Noble gas-water interaction</i>		
He-O	2.9730	0.20500
Ne-O	2.9758	0.45416
Ar-O	3.2645	0.86608
Kr-O	3.3948	0.98380
Xe-O	3.5874	1.07990
<i>Water-water interaction (Berendsen et al., 1987)</i>		
O-O	3.1656	0.65017

Table 3. Location of the first maximum and minimum of  $g_{NGO}(r)$  and first-shell coordination number of O atoms around noble gas solutes in ambient liquid water. Confidence intervals on  $r_{\max}$  and  $r_{\min}$  values are  $\pm 0.05$  Å.

Noble gas	$r_{\max}$ (Å)	$r_{\min}$ (Å)	$n^O$
He	3.0	4.7	$14.0 \pm 0.4$
Ne	3.1	4.9	$15.7 \pm 0.4$
Ar	3.5	5.2	$18.8 \pm 0.5$
Kr	3.7	5.4	$21.2 \pm 0.5$
Xe	3.9	5.6	$22.4 \pm 0.5$



Table 4. Self-diffusion coefficients of noble gas isotopes with  $m = 4\text{-}132$  Da in ambient liquid water. Confidence intervals ( $\pm 2\sigma$ ) were estimated from  $D$  values obtained for twenty 0.4 ns ‘blocks’ of each 8 ns simulation.

$m$	$D_{\text{He}}$	$D_{\text{Ne}}$	$D_{\text{Ar}}$	$D_{\text{Xe}}$
(Da)	( $10^{-9} \text{ m}^2 \text{ s}^{-1}$ )	( $10^{-9} \text{ m}^2 \text{ s}^{-1}$ )	( $10^{-9} \text{ m}^2 \text{ s}^{-1}$ )	( $10^{-9} \text{ m}^2 \text{ s}^{-1}$ )
4.0026	$7.85 \pm 0.54$	$5.94 \pm 0.32$	$2.93 \pm 0.21$	$1.93 \pm 0.10$
19.9924	$6.17 \pm 0.40$	$4.78 \pm 0.37$	$2.66 \pm 0.15$	$1.91 \pm 0.14$
39.9624	$5.48 \pm 0.26$	$4.23 \pm 0.31$	$2.57 \pm 0.15$	$1.77 \pm 0.09$
131.9041	$4.28 \pm 0.24$	$3.52 \pm 0.22$	$2.21 \pm 0.18$	$1.57 \pm 0.11$

Table 5. Parameters of the linear regression equation  $\log D = A - \beta \cdot \log m$  calculated with 16 paired  $D, m$  values for each noble gas solute.

Solute	$A$	$\beta$
He	$1.00 \pm 0.04$	$0.171 \pm 0.028$
Ne	$0.87 \pm 0.03$	$0.150 \pm 0.018$
Ar	$0.52 \pm 0.04$	$0.078 \pm 0.024$
Xe	$0.33 \pm 0.03$	$0.059 \pm 0.023$

## List of Figures

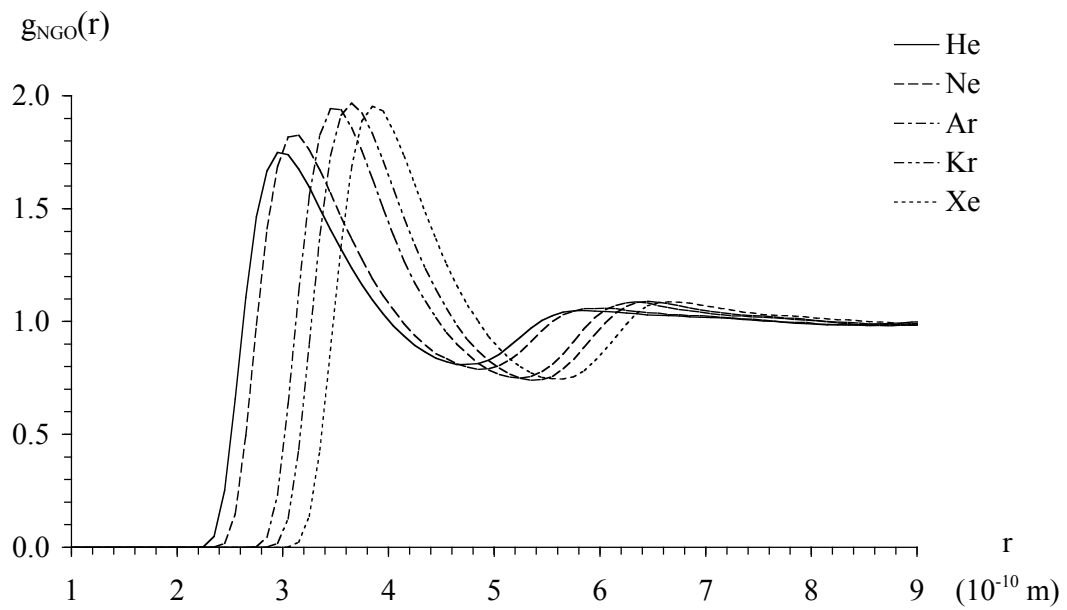
Fig. 1. Radial distribution functions of (a) O atoms and (b) H atoms near noble gases in liquid water at 298 K.

Fig. 2. Snapshot of a  $^{40}\text{Ar}$  atom (in green) and water molecules located in its first solvation shell (i.e., at Ar-O distances  $< 5.2 \text{ \AA}$ ). Highlighted water molecules in the upper and lower parts of the figure illustrate the two possible ‘straddling’ configurations, with either a lone pair of electrons (upper part of the figure) or an H atom (lower part of the figure) pointing away from the solute.

Fig. 3. Experimental and simulated data on noble gas solvation structure in liquid water at 298 K: (a) Kr-O radial distribution function [experimental results were obtained at 20 bar; confidence intervals on experimental results ( $\pm 0.3$ ) are shown as vertical error bars (Bowron et al., 1998)] and (b) Ar total distribution function [experimental results were obtained at  $\sim 240$  bar; vertical and horizontal confidence intervals on experimental results ( $\pm 2\sigma$ ) are based on two replicates of  $G_{\text{Ar}}$  reported by Broadbent and Neilson (1994)].

Fig. 4. Diffusion coefficients of hypothetical 4 Da and 132 Da isotopes of four noble gases (from left to right: Xe, Ar, Ne and He) plotted as a function of inverse solute radius ( $1/r, \text{ \AA}^{-1}$ ). The dashed lines are power-law relations fitted to the simulation results. The solid line was calculated with the Stokes-Einstein relation [with  $\mu = 0.894 \text{ Pa s}^{-1}$  at 298 K (Bingham et al., 1913)].

a)



b)

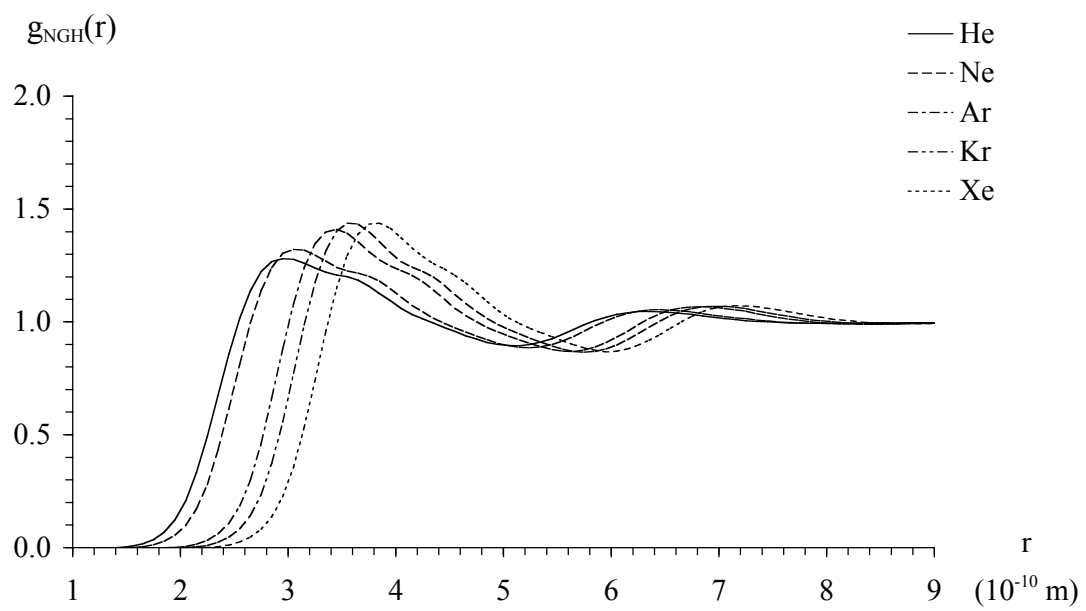


Figure 1.

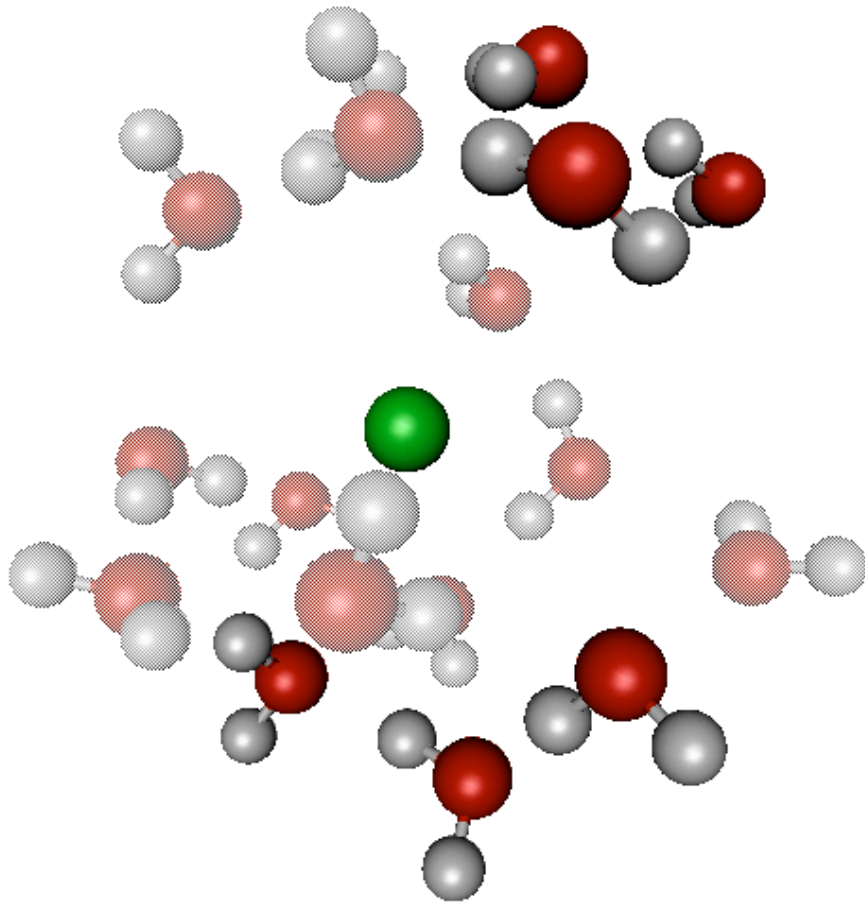
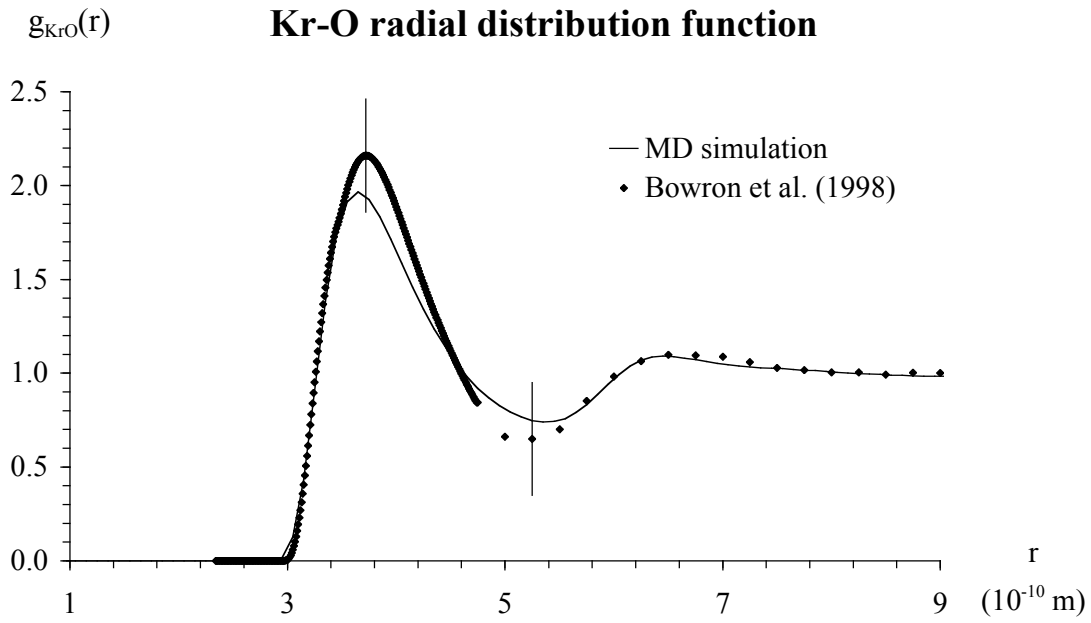


Figure 2.

a)



b)

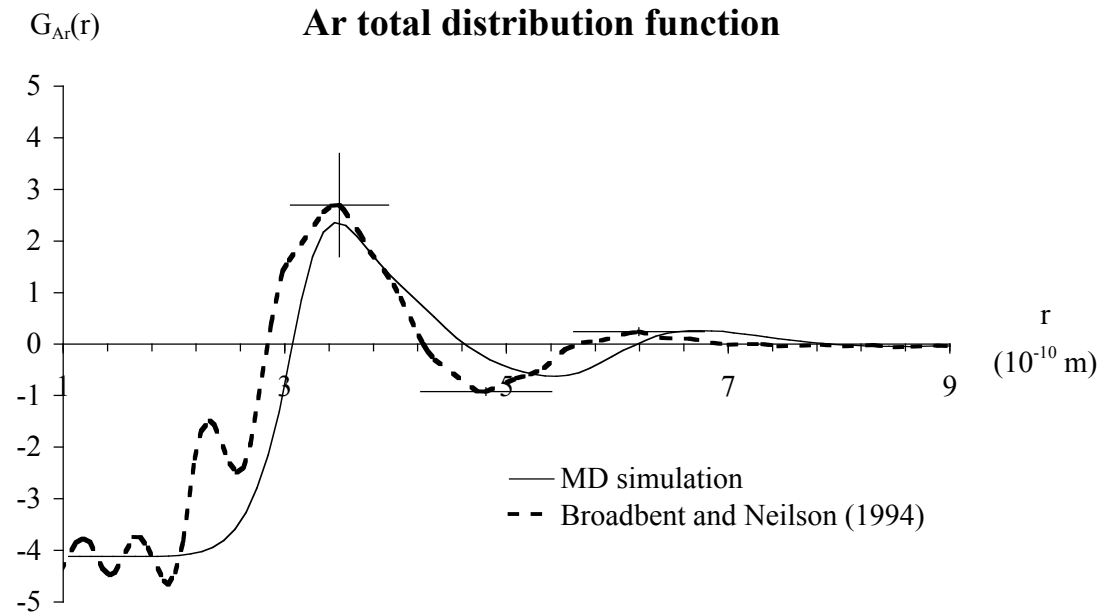


Figure 3.

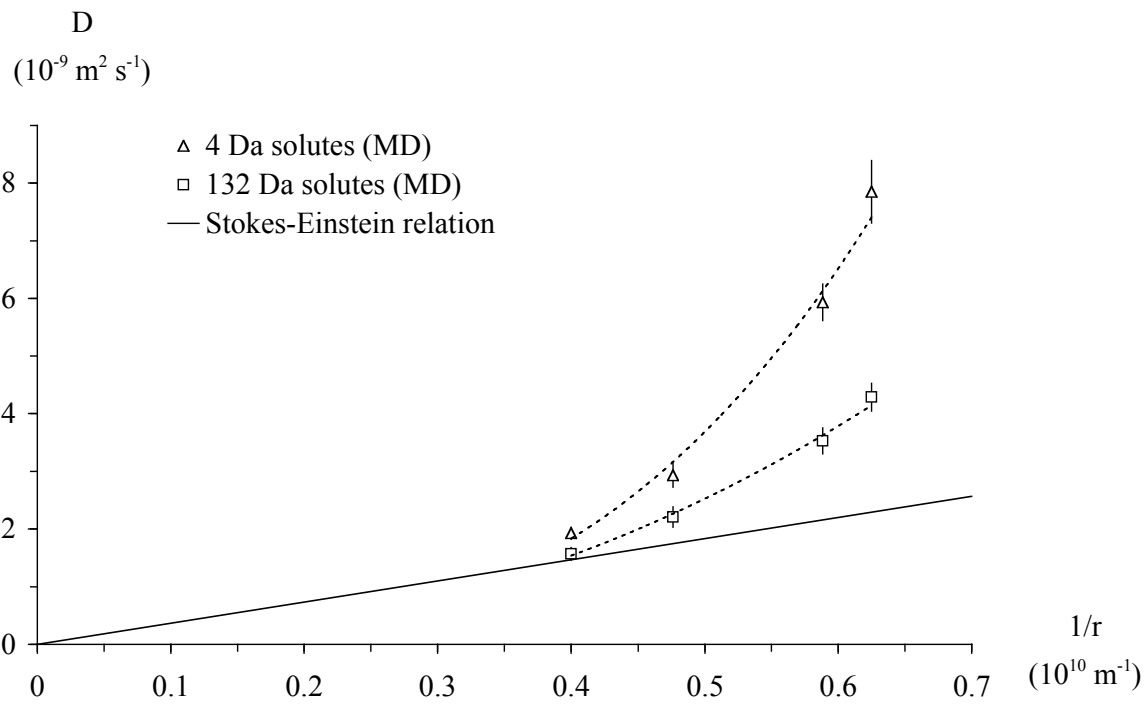


Figure 4.