Molecular dynamics simulations of noble gases in liquid water: Solvation structure, self-diffusion, and kinetic isotope effect

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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 so 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 proven to be important geochemical indicators of transport processes and paleoclimate in hydrogeological basins (1-7), lacustrine sediments (8-10), aquitards (11-13), engineered clay barriers (14) and the oceans (15). Brennwald et al. (10) used Ne, Ar, Kr and Xe concentrations and $^{20}Ne/^{22}Ne$ and $^{36}Ar/^{40}Ar$ isotopic ratios to estimate rates of methane release from anoxic lake sediments. Rübel et al. (12) used ^{4}He concentrations and $^{40}Ar/^{36}Ar$ 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. (1) 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. (1), 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 (1, 3). For each noble gas other than Ne, the mass fraction released during the third step ($1\text{-}f_{NG}$) is related to the mass fraction of neon released during the third step ($1\text{-}f_{\mathrm{Ne}}$) by the well-known Rayleigh fractionation formula (if D_{NG} is the self-diffusion coefficient of a noble gas in water):

$$f_{NG} = f_{\mathrm{Ne}}^{\,D_{NG}/D_{\mathrm{Ne}}} \qquad [1]$$

Pore water concentrations of the four noble gases Ne, Ar, Kr and Xe then allow the calculation of the four unknown parameter-values: ground temperature and atmospheric pressure at the time and location of groundwater recharge, total amount of dissolved 'excess air', and f_{Ne} (1, 3).

Paleotemperatures calculated in this way are most sensitive to Xe concentrations, because the temperature-dependence of noble gas solubility increases with atomic mass (3).

Despite the importance of noble gas diffusion coefficients in low-temperature geochemistry, remarkably few measurements of these critical parameters have been reported. Jähne et al. (16) measured self-diffusion coefficients of four noble gases in liquid water at 298 K (Table 1). Pulsed field gradient nuclear magnetic resonance (PFG NMR) studies (17, 18) confirmed the result of Jähne et al. (16) for Ne diffusion, but yielded a significantly larger Xe self-diffusion coefficient (18). No other experimental data on noble gas diffusion in liquid water appear to have been published during the last twenty years. Data on the self-diffusion coefficients of minor noble gas isotopes are even more scarce: they consist of a single measurement of the ratio of the self-diffusion coefficients of ^{3}He and ^{4}He: $D(^{3}\mathrm{He})/D(^{4}\mathrm{He}) = 1.15 \pm 0.03$ (16).

With this extreme paucity of experimental data, most geochemical studies of noble gas solutes have relied upon the He, Ne, Kr and Xe diffusion coefficients measured by Jähne et al. (16) together with Ar diffusion coefficients estimated by extrapolation of the results of Jähne et al. (16) (1, 3-6, 8-13, 15, 19). Self-diffusion coefficients of minor noble gas isotopes in liquid water for which no data exist then have routinely been estimated using the kinetic-theory model $D \propto 1/\mu^{0.5}$ [μ is the solvent-solute reduced mass, $\mu = mm_0/(m + m_0)$, if m and m_0 are solute and solvent molecular masses (7)] or, more commonly, the relation $D \propto 1/m^{0.5}$, which is obtained from the kinetic-theory model under the assumption that the hydrogen-bonded water network behaves as an 'effective particle' of infinitely large mass ($m_0 >> m$) (4, 6, 9, 10, 19). Use of the relation $D \propto 1/m^{0.5}$ in conjunction with measured ^{20}Ne/^{22}Ne or ^{36}Ar/^{40}Ar solute isotopic ratios in porous media has led to a widespread dismissal of diffusion in pore water as a significant

79 contributor to noble gas transport (4, 6, 10, 19) and, in particular, to strong dismissal (4, 19) of
80 the paleotemperature reconstruction method developed by Stute et al. (1).
81 Very recently Richter et al. (20) discovered somewhat unexpectedly that the self-diffusion
82 coefficients of ionic solutes in liquid water do not follow the 'square-root' model in their
83 dependence on isotopic mass. They provided the first precise measurements of the kinetic
84 fractionation of Mg, Li, and Cl isotopes by diffusion in liquid water and showed that a more
85 general inverse power-law relation, $D \propto m^{-\beta}$, was applicable, with $\beta_{Mg} \sim 0$, $\beta_{Li} = 0.0148 \pm 0.0017$
86 and $\beta_{Cl} = 0.026 \pm 0.014$. Our subsequent molecular dynamics (MD) simulations of the self-
87 diffusion of these ions (21) fully corroborated the small experimental β-values and provided
88 insight based on hydration shell dynamics as to why β differed among the three ions.
89 The very low solubility of noble gases in ambient water currently prevents the use of the
90 experimental method of Richter et al. (20) to measure the mass-dependence of their self-
91 diffusion coefficients (F. M. Richter, personal communication, 2006). The self-diffusion
92 coefficients of noble gas isotopes in liquid water can be calculated, however, by MD simulation.
93 The accuracy of simulations performed for this purpose is limited mainly by the quality of the
94 water-water and noble gas-water intermolecular potentials used. Previous molecular simulations
95 of noble gas solutes in ambient water (22-29) have incorporated noble gas-water potentials
96 calculated either from somewhat outdated noble gas-noble gas interaction data (30) or with
97 approximate (Lorentz-Berthelot) combining rules. Noble gas-water potentials used in these
98 studies were tested only by comparing model predictions with experimental data on the enthalpy
99 and Gibbs energy of hydration. Gibbs energies of noble gas solvation in ambient water were
100 predicted with about 4 kJ mol^{-1} inaccuracy; however, the Gibbs energies of solvation of Ne and

101 Xe differ by only 4.3 kJ mol^{-1} (28). The simulated noble gas self-diffusion coefficients (29) in
102 fact overestimated most experimental data (Table 1).
103 In the present study, MD simulations of noble gas solutes in liquid water were carried out
104 with a new set of noble gas-water potentials calculated with noble gas-noble gas interaction data
105 (31, 32) that are more recent than those of Hirschfelder et al. (30) and with combining rules that
106 are more accurate than the Lorentz-Berthelot rules (33). Our results for the major noble gas
107 isotopes (^{4}He, ^{20}Ne, ^{40}Ar, ^{84}Kr, ^{132}Xe) corroborate available data on their solvation structure (34,
108 35) and self-diffusion coefficients in ambient water (16, 17). Simulations following the
109 methodology of Bourg and Sposito (21) also were performed to determine the isotopic mass-
110 dependence of noble gas self-diffusion coefficients.
111
112 **Solvation structure**
113 The solvation structure near ^{4}He, ^{20}Ne, ^{40}Ar, ^{84}Kr and ^{132}Xe in ambient liquid water as revealed by
114 radial distribution functions is summarized in Figure 1 [radial distribution functions for O and H
115 atoms near noble gas solutes, $g_{NGO}(r)$ and $g_{NGH}(r)$] and Table 2 [location of the first maximum
116 (r_{max}) and minimum (r_{min}) of each $g_{NGO}(r)$ function, and average number of water molecules in the
117 first solvation shell (N_{shell})]. The slightly shorter first-shell peak distance in $g_{NGH}(r)$ as compared
118 to $g_{NGO}(r)$ indicates that first-shell water molecules are preferentially oriented in a "straddling"
119 configuration, such that one of the apices of the water tetrahedron points away from the noble
120 gas atom (36, 37) (Figure 2). This preferred configuration, however, does not require the
121 existence of a static clathrate cage: it exists even for small hydrophobic solutes (H, He, Ne) that
122 diffuse much more rapidly than nearby water molecules and have a 'floppy' solvation shell (38).
123 Radial distribution functions for the smallest noble gas atoms, He and Ne, (Figure 1) are similar

to those obtained by Kirchner et al. (38) by *ab initio* MD simulation of a solvated uncharged H atom. The evident absence of solvation structure beyond the first shell is consistent with previous MD simulation studies (23, 25).

No experimental data appear to be available concerning the solvation structure around noble gases in ambient liquid water. Bowron et al. (35) used extended X-ray absorption fine-structure (EXAFS) spectroscopy to determine the radial distribution function of O atoms around Kr in water at 20 bar and 277 to 348 K. If the results of Bowron et al. (35) are extrapolated to ambient pressure, based on the lack of pressure-dependence of Kr solvation structure in water between 20 to 700 bar (39, 40), they are in good agreement with our MD simulation results (data not shown). Broadbent and Neilson (34) calculated the total distribution function of argon [$G_{\mathrm{Ar}}(r)$] in D_2O at 298 K and ~240 bar from isotopic-difference neutron diffraction data on natural Ar ($^{\mathrm{Nat}}$Ar) and ^{36}Ar aqueous solutions. The total distribution function is related to the partial radial distribution functions by:

$$G_{Ar}(r) = A\left[g_{NGO}(r) - 1\right] + B\left[g_{NGH}(r) - 1\right] + C\left[g_{\mathrm{ArAr}}(r) - 1\right] \qquad [2]$$

where the weighting coefficients have the values $A = 1.247$, $B = 2.869$ and $C \approx 0$ at 240 bar (34). Our MD simulation of G_{Ar} based on the partial radial distribution functions is also consistent with the experimental G_{Ar} (data not shown).

Self-diffusion coefficients

Experimental and simulation results on the self-diffusion coefficients of major noble gas isotopes in water at 298 K are shown in Table 1 and Figure 3. The self-diffusion coefficients predicted in the present study are consistent with the experimental data of Jähne et al. (16). Notably, our Xe simulation results support the experimental results of Jähne et al. (16), not those of Weingärtner

et al. (18). Our Ar simulation results also are consistent with D_{Ar} values estimated by extrapolation of the He, Ne, Kr and Xe diffusion data of Jähne et al. (16) [$D_{Ar} = 2.66 \times 10^{-9}$ m^2 s^{-1} at 298 K (4)].

Kinetic fractionation by diffusion in liquid water

The mass dependencies of the self-diffusion coefficients of noble gas isotopes as obtained by MD simulation were analyzed by plotting average log D values obtained during four 2 ns 'blocks' of each 8 ns simulation vs. log m. Linear regression of the data shows that the isotopic mass-dependence of noble gas self-diffusion coefficients has the generic power-law form:

$$D \propto m^{-\beta} \qquad [3]$$

with $\beta > 0$, as proposed originally for ionic solutes by Richter et al. (20) (Linear regression of simulation results as log D vs. log μ yielded a poorer fit than equation 3 for He, Ne, Ar and Xe). The linear regression parameters obtained with equation 3 (Table 3) indicate that $\beta < 0.2$, in stunning contradiction with the kinetic theory model $D \propto 1/m^{0.5}$ (4, 6, 9, 10, 19). For 'Brownian' particles (i.e., solutes that are much larger and heavier than the solvent molecules), the well-known Stokes-Einstein relation predicts that the self-diffusion coefficient should be independent of isotopic mass (i.e., $\beta = 0$ in equation 3). The decrease in β-values in the order He $\geq$ Ne > Ar $\geq$ Xe that we observed suggests that the larger noble gas solutes indeed behave in a more 'Brownian' manner than do the smaller noble gas solutes. If the solute radius r (Å) is estimated as r_{max} for g_{NGO} (Table 2) minus half of r_{max} for the O-O radial distribution function in pure water (1.4 Å), then our β-values are well described by the power-law relation $\beta = B\,(1/r)^{\gamma}$ with $B = 0.55 \pm 0.17$ and $\gamma = 2.49 \pm 0.45$ ($R^2 = 0.98$).

Conclusions

A new set of noble-gas water interaction parameters, derived with improved combining rules and noble gas-noble gas interaction parameters, allowed successful prediction of all available experimental data on the solvation structure and self-diffusion coefficients of major noble gas isotopes in ambient liquid water. In particular, our simulation results corroborate the self-diffusion coefficients of major noble gas isotopes measured by Jähne et al. (16) that are widely used in geochemical studies (1, 3-6, 8-13, 15, 19). Our MD simulations carried out with a broad range of solute isotopic masses revealed that noble gas self-diffusion coefficients in water follow an inverse power-law mass-dependence, $D \propto m^{-\beta}$, with $0 < \beta < 0.2$. Thus, the commonly invoked 'square root' model of noble gas isotope fractionation by diffusion in liquid water (4, 6, 9, 10, 19) overestimates the strength of the mass-dependence of noble gas self-diffusion coefficients.

Simulation methods

Molecular dynamics simulations (8 ns interval, preceded by 202 ps of equilibration at 298 K) were carried out with the program MOLDY 3.6 (41) for one noble gas atom and 550 water molecules in a periodically replicated, cubic cell (microcanonical ensemble, 0.997 kg dm^{-3} density) with the methodology of Bourg and Sposito (21). Molecular trajectories were calculated by solving the Newton-Euler equations (with a 1 fs time step) with a form of the Beeman algorithm, the most accurate of all "Verlet-equivalent" algorithms (41). Long-range interactions were treated by Ewald summation with parameters chosen to yield an Ewald sum accuracy of 99.99%. Total energy drift during each 8 ns simulation was about 0.002 %. Liquid water was described with the extended simple point charge (SPC/E) model of Berendsen et al. (42). Despite its simplicity [fixed O-H bond lengths (1 Å), H-O-H angle (109.47°) and atomic charges (q_O = -

193 0.8476 e and q_H = 0.4238 e)] the SPC/E model predicts the self-diffusion coefficient of water at
194 298 K to within 4 ± 17 % (43), the static dielectric constant of water at 324.2 and 523 K (at 1 kg
195 dm^{-3} density) to within 2 ± 20 and 4 ± 8 % (44), and the X-ray scattering intensities of liquid
196 water at 298 and 350 K to within 1.8 % (45).

197 On the SPC/E model, short-range non-Coulombic interactions (ϕ_{ij}, kJ mol^{-1}) between water O
198 atoms are described with the Lennard-Jones (LJ) 6-12 model:

199 $$\phi_{ij}\left(r_{ij}\right) = 4 \in_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12}\right] \qquad [3]$$

200 where r_{ij} (Å) is the interatomic distance and $2^{1/6}\sigma_{ij}$ and $\in_{ij}$ are the location (Å) and depth of the
201 potential well (J mol^{-1}). The LJ 6-12 model, with noble gas σ_{ii} and $\in_{ii}$ parameters compiled by
202 Aziz (31), accurately describes interactions between noble gas atoms in the region of the
203 potential well (32). In the present study, σ_{ij} and $\in_{ij}$ parameters for the interaction between noble
204 gases and water O atoms were calculated from noble gas and SPC/E water σ_{ii} and $\in_{ii}$ parameters
205 with the combining rules of Kong (33):

206 $$\in_{ij} \sigma_{ij}^{6} = \sqrt{\in_{ii} \sigma_{ii}^{6} \cdot \in_{jj} \sigma_{jj}^{6}} \qquad [4a]$$

207 $$\in_{ij} \sigma_{ij}^{12} = \left[\frac{\left(\in_{ii} \sigma_{ii}^{12}\right)^{1/13} + \left(\in_{jj} \sigma_{jj}^{12}\right)^{1/13}}{2}\right]^{13} \qquad [4b]$$

208 Equations 4a,b, combined with the kinetic theory of gases, predict self-diffusion coefficients in
209 binary mixtures of noble gases with less than 2 % inaccuracy in a broad temperature range (300
210 to 1400 K), except for Ar-Kr mixtures (33). The same diffusion data, however, are poorly
211 predicted if σ_{ij} and $\in_{ij}$ are calculated with the Lorentz-Berthelot rules (46). The Lennard-Jones
212 parameters used in the present study are compiled in Table 4.

Simulations were carried out with ^{4}He, ^{20}Ne, ^{40}Ar, ^{84}Kr and ^{132}Xe isotopes to test the quality of the noble gas-water interaction potentials in Table 4, and with a range of hypothetical isotopes of He, Ne, Ar and Xe (m = 4-132 Da) to determine the isotopic mass dependence of solute self-diffusion coefficients. Previous studies have used MD simulation with a broad range of solute mass to infer solute isotopic effects, mainly in Lennard-Jones or hard-sphere fluids (47-49) but also in liquid water (21, 50, 51). Radial distribution functions of O and H atoms near noble gas (NG) solutes and noble gas velocity autocorrelation functions ($\langle \mathbf{v}(0)\cdot\mathbf{v}(t)\rangle$) were calculated with standard methods (41, 52). The average number of oxygen atoms in the first solvation shell of each noble gas (N_{shell}) was calculated by integrating the function $4\pi r^2 g_{NGO}(r)$ to its first minimum (r_{min}). Solute self-diffusion coefficients were calculated with the well-known Green-Kubo relation (52):

$$D = \frac{1}{3}\lim_{\tau\to\infty}\int_0^{\tau}\left\langle \mathbf{v}(0)\cdot\mathbf{v}(t)\right\rangle dt \qquad [5]$$

The 'infinite limit' in equation 5 was approximated accurately by taking the average of D-values obtained for τ = 2.4 to 2.5 ps.

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

Noble gas	Experimental (16)	Experimental (17, 18)	MD simulation (29)	MD simulation (this study)
He	7.22 ± 0.36		10.0 ± 0.9	7.85 ± 0.54
Ne	4.16 ± 0.21	4.18 ± 0.20	4.9 ± 0.2	4.78 ± 0.37
Ar			2.4 ± 0.1	2.57 ± 0.15
Kr	1.84 ± 0.09		2.1 ± 0.1	1.97 ± 0.13
Xe	1.47 ± 0.07	1.90 ± 0.09[a]	1.6 ± 0.1	1.57 ± 0.11

[a] confidence interval calculated with the assumption that NMR data for Ne and Xe diffusion have similar coefficients of variation.

Table 2. 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 ± 0.05 Å.

Noble gas	r_{max} (Å)	r_{min} (Å)	N_{shell}
He	3.0	4.7	14.0 ± 0.4
Ne	3.1	4.9	15.7 ± 0.4
Ar	3.5	5.2	18.8 ± 0.5
Kr	3.7	5.4	21.2 ± 0.5
Xe	3.9	5.6	22.4 ± 0.5

Table 3. 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.

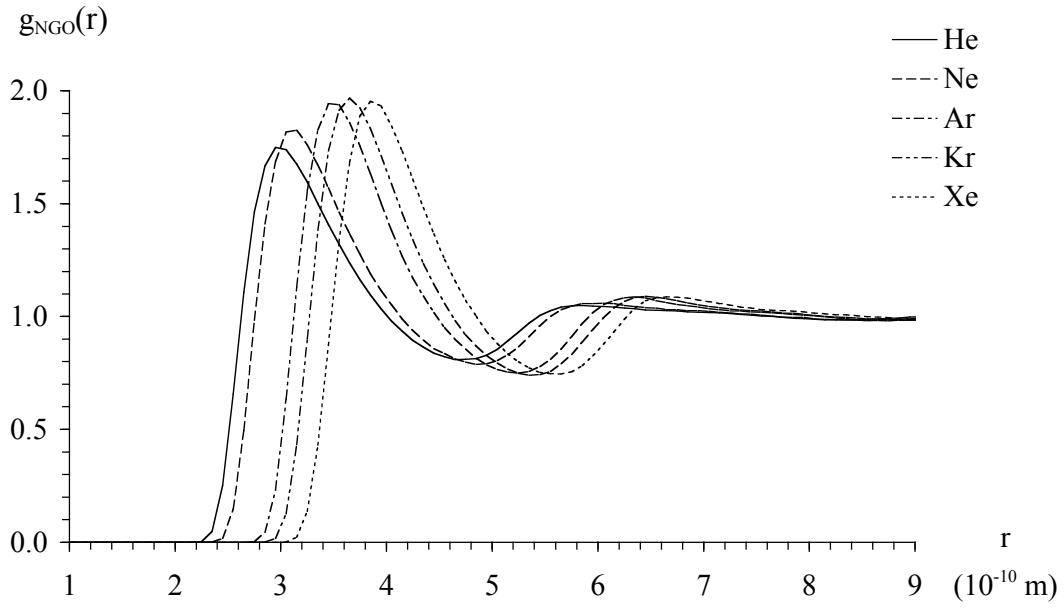
Solute	A	β	R^2
He	1.00 ± 0.04	0.171 ± 0.028	0.91
Ne	0.87 ± 0.03	0.150 ± 0.018	0.95
Ar	0.52 ± 0.04	0.078 ± 0.024	0.75
Xe	0.33 ± 0.03	0.059 ± 0.023	0.65

Table 4. Lennard-Jones 6-12 potential parameters.

Atom pair	σ (Å)	∈ (kJ mol^{-1})
Noble gas-water interaction		
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
Water-water interaction (42)		
O-O	3.1656	0.65017

List of Figures

a)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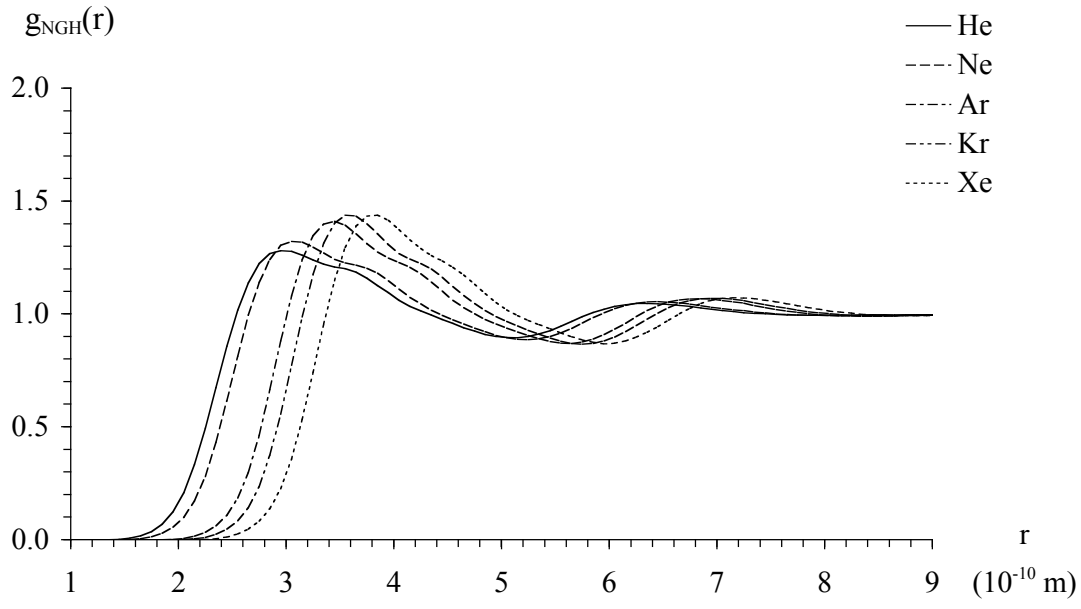
b)


$g_{NGH}(r)$
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(10^{-10} m)

Figure 1.

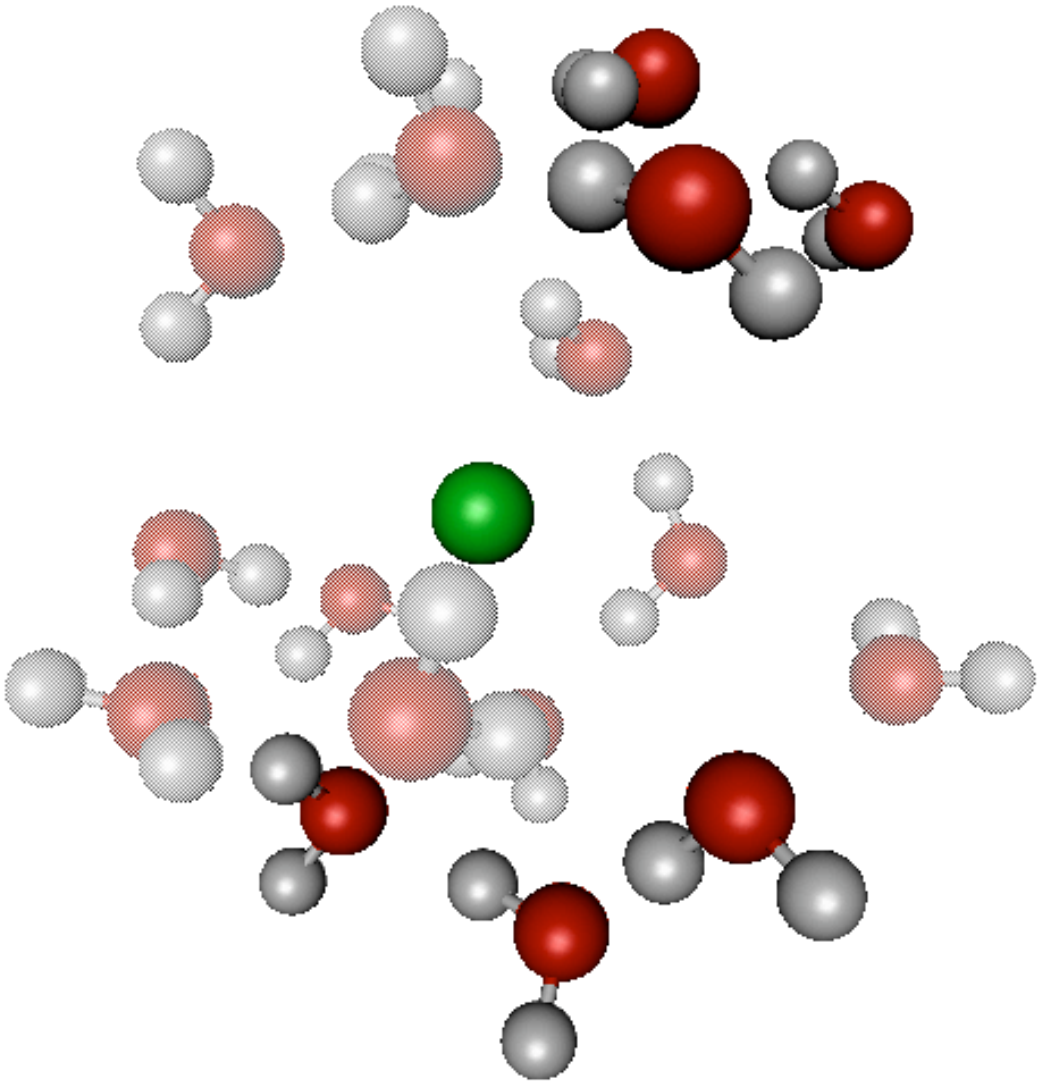

Figure 2.

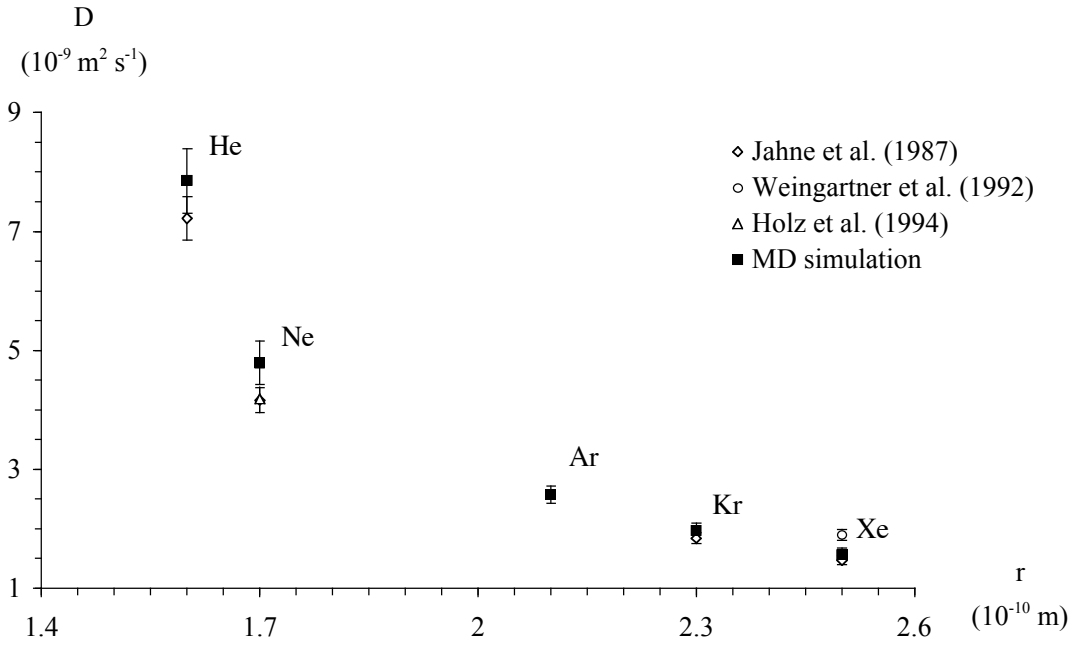
D
(10-9 m2 s-1)
9
7
5
3
1
He
Ne
Ar
Kr
Xe
Jahne et al. (1987)
Weingartner et al. (1992)
Holz et al. (1994)
MD simulation
1.4
1.7
2
2.3
2.6
r
(10-10 m)

Figure 3.