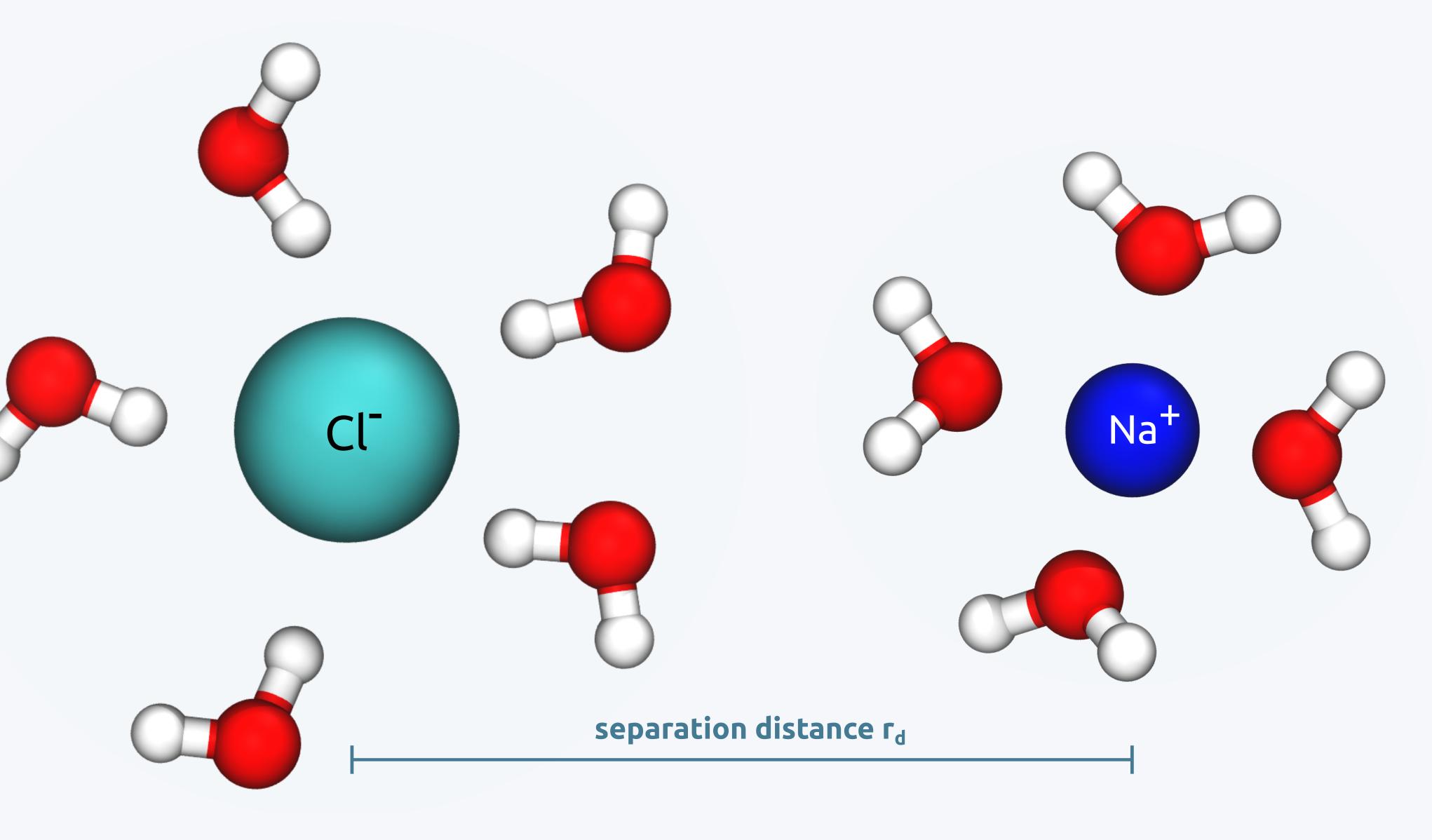


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Ion Dissociation in Water Under Supercritical Conditions: A Molecular Perspective on Linear Density Models for Equilibrium Constants

1. Introduction

Experiments shown linear have 9 **dependence** between the logarithms of the H₂O density (log(p)) and equilibrium supercritical constants (log(K)) at conditions. This is a promising basis for future thermodynamic models [1]. Here we test the empirically found linearity using the example of **NaCl** with the help of **classical** molecular dynamics (MD) simulations. Our approach is based on the following relationship:

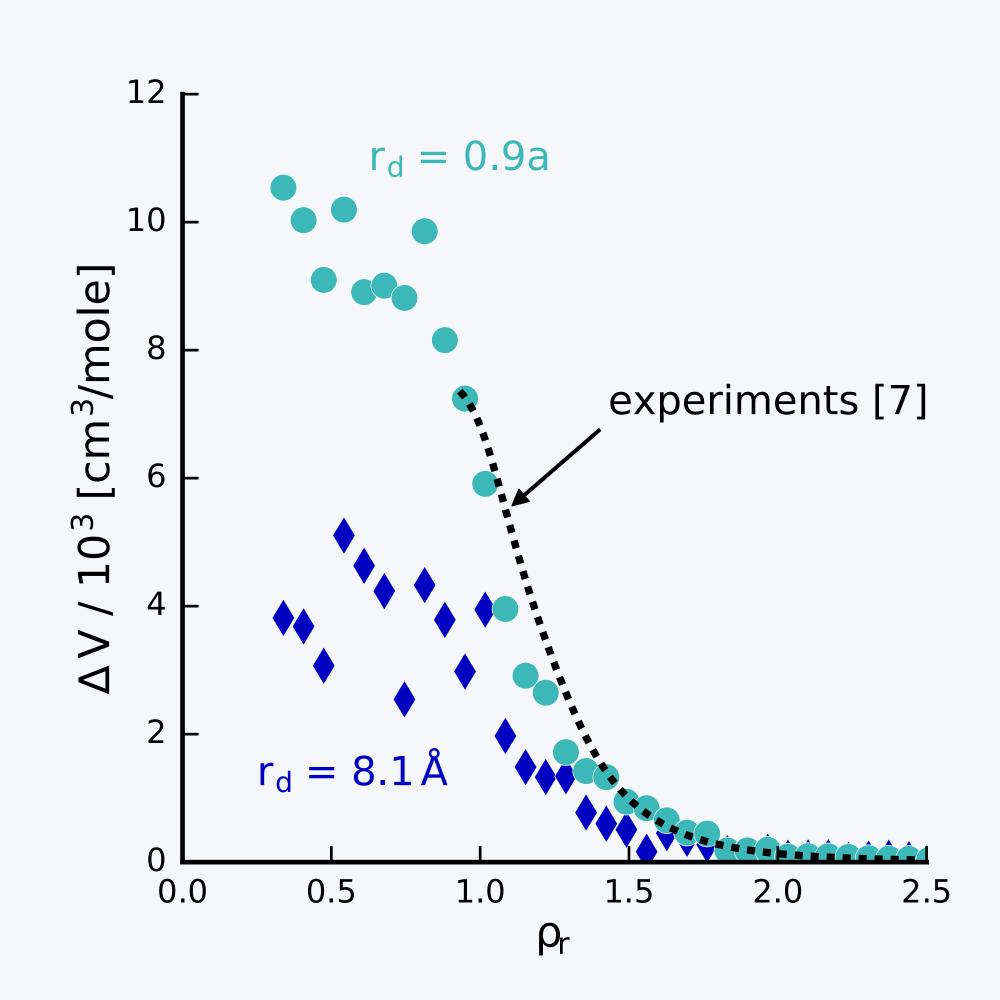


 $\mathbf{k} = \frac{\partial \log(\mathbf{K})}{\partial \log(\rho)} = \frac{\Delta \mathbf{V}}{\beta \mathbf{RT}}$

where ΔV is the volume of reaction, R is the gas constant, T is the temperature and β is the compressibility of H₂O [2].

2. Methods

Classical MD simulations were carried out with the LAMMPS code [3]. The TIP4P/2005 model [4] and force field parameters from Joung & Cheatham [5] were used to describe



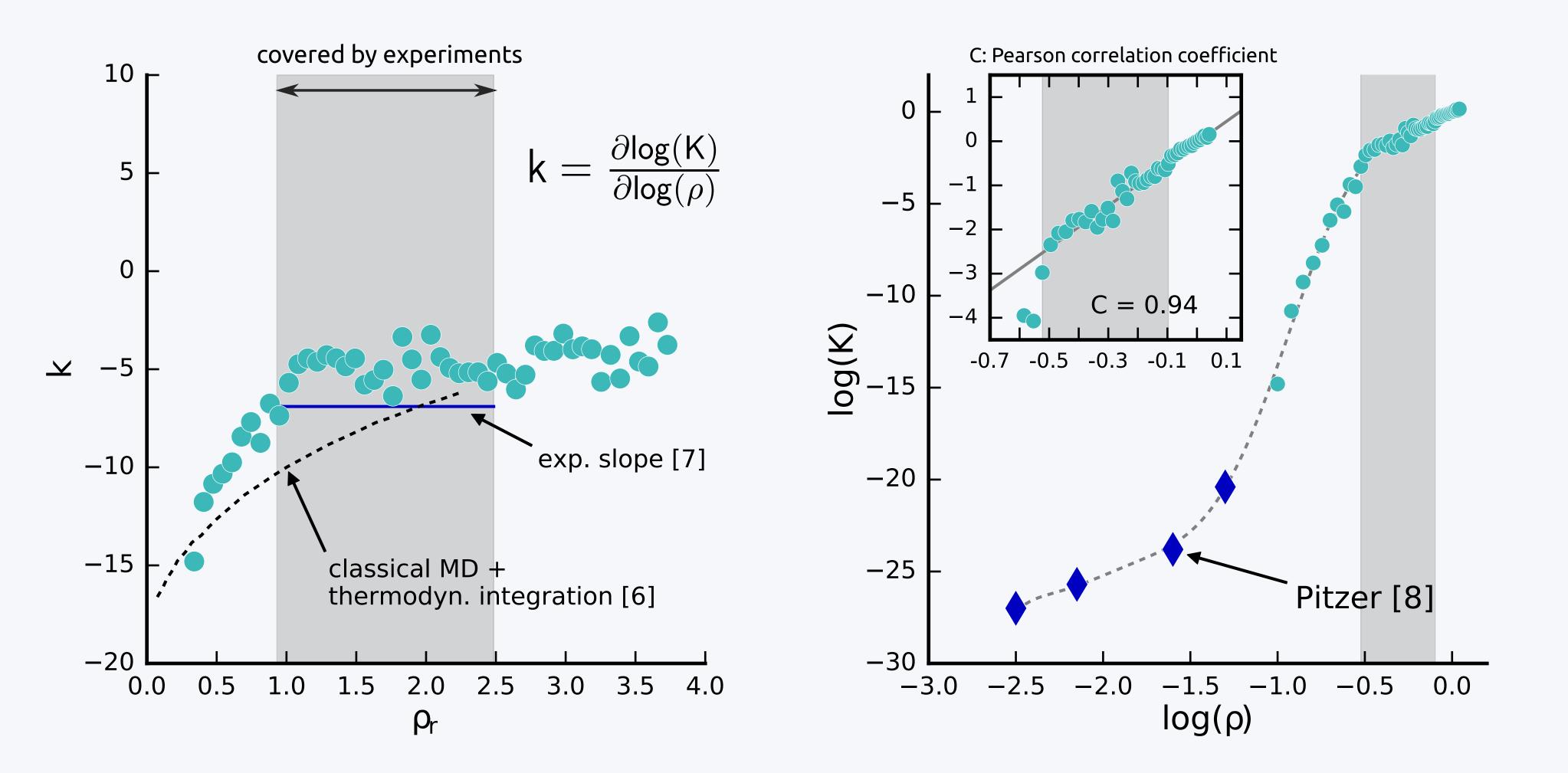
3. Volume of Reaction

The question of the **distance** \mathbf{r}_d at which a **pair of ions** is considered **dissociated** is not trivial in the case of supercritical aqueous fluids. Therefore, we tested two different

H₂O and NaCl. The system consists of 2056 H₂O molecules and one NaCl ion pair. β and ΔV were determined by simulations in the isothermal-isobaric (NPT) ensemble at **673** K and **pressures from 16 to 1269 MPa**, corresponding to **densities of 0.1 to 1.1 g/cm³**. For comparability, the results are presented as a function of the reduced density $\rho_r = \rho/\rho_c$, where ρ_c is the density of H₂O at the critical point. cases. First, a series of simulations was performed with \mathbf{r}_d set constant at **8.1** Å, a typical value used in previous studies [6]. In the second series, \mathbf{r}_d was set to **0.9a**, where **a is half the length of the simulation cell**. The dependence of ΔV on \mathbf{r}_d increases with decreasing ρ_r (left figure). ΔV matches experimental data [7] much better for the higher separation distance $\mathbf{r}_d = 0.9a$.

4. Discussion

For $r_d = 0.9a$, k is constant at $\rho_r > 1$ (first figure to the right). This **confirms the empirically found linear relationships**. The relatively large separation length r = 0.9a is necessary to account for the long-ranged solute-solvent interactions near the critical



point of H_2O . At $\rho_r < 1$, k decreases to smaller values. The resulting values for log(K) form an s-shaped curve with values calculated for the vapour phase as predicted by Pitzer [8] decades ago! Furthermore, the linearity between log(K) and log(ρ) also seems to hold at higher ρ .

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