

Ionic Conductivity & Solvation Dynamics of NaCl

A Molecular Dynamics Study (0.5 M – 1.8 M)

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Simulation Details (1.0 M Run)

Parameter	Value / Notes
Software	GROMACS 2024.5
System	39 Na ⁺ , 39 Cl ⁻ , 2084 Water (1.0 M)
Box	≈ 4 nm cubic box
Force fields	GROMOS 54A7 (Ions), SPC/E (Water)
Ensemble	NVT (100 ps) → NPT (100 ps) Equil. NPT Production (100 ns run)
Timestep	2 fs (constraints = all-bonds)
Electrostatics	PME, cutoff = 1.0 nm
Thermostat	V-rescale (T = 298 K)
Barostat	Parrinello-Rahman (P = 1 bar)
GK Analysis	gmx current (from 10 fs .trr file)
NE Analysis	gmx msd (from unwrapped .xtc)
Structure	gmx rdf, gmx select -olt

Methodology and best practices adapted from Weitzner *et al.* [?]

Methodology: Green-Kubo Conductivity

- 1. The Theory** Electrical conductivity (σ) is calculated from the fluctuations of the total electric current $\mathbf{J}(t)$ in the system at equilibrium.
- 2. The Current Vector** At every time step, we sum the charge-weighted velocities of all ions:

$$\mathbf{J}(t) = \sum_{i=1}^N q_i \mathbf{v}_i(t)$$

- 3. The Green-Kubo Integral** Conductivity is the time integral of the Current Autocorrelation Function (ACF):

$$\sigma_{GK} = \frac{1}{3Vk_B T} \int_0^\infty \langle \mathbf{J}(t_0) \cdot \mathbf{J}(t_0 + t) \rangle dt$$

Note: This method captures ion-ion correlations (like pairs moving together), making it rigorous for concentrated solutions, unlike Nernst-Einstein.

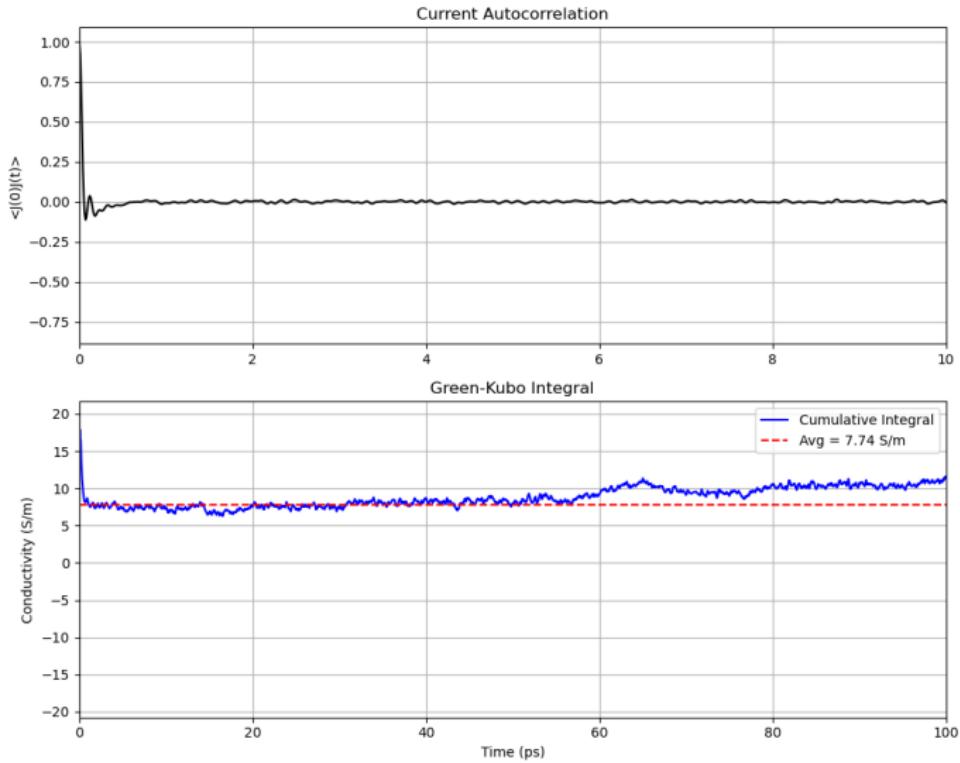


Figure: Current ACF and Conductivity Integral.

Green-Kubo Convergence Analysis

Interpreting the Plot:

- **Top Panel (ACF):** Shows how quickly the memory of the current decays.
 - The sharp drop at < 1 ps indicates rapid randomization of ion velocities by the solvent.
- **Bottom Panel (Integral):** The cumulative conductivity.
 - The curve rises initially and then settles into a **Plateau**.
 - The average value of this plateau is reported as σ_{GK} .

1. Electrical Conductivity Data

Green-Kubo Results (GROMOS 54A7 / SPC/E)

Concentration (M)	Simulated σ_{GK} (S/m)
0.5	4.74(exp - 4.78)
0.8	7.74
1.0	8.60
1.2	9.08
1.5	10.86
1.8	13.07

Conductivity Trend

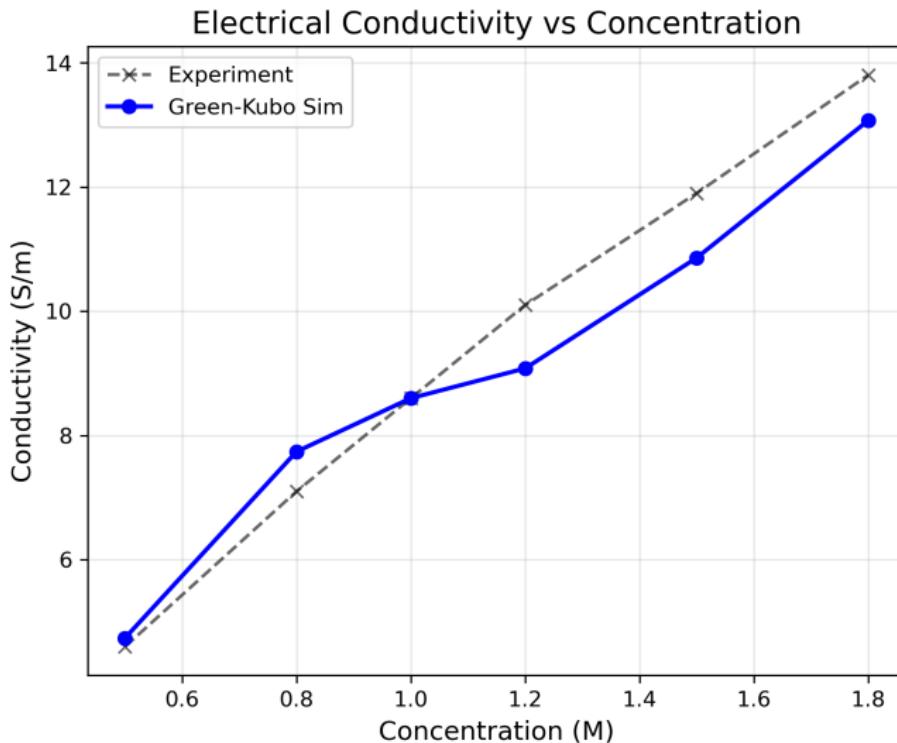


Figure: Green-Kubo Conductivity vs. Concentration.

Analysis: Conductivity Trends

Observations:

- The trend is strictly linear in this concentration regime ($\sigma \propto c$).
- **No Saturation:** Up to 1.8 M, the increase in the number of charge carriers (N_{ions}) dominates the transport.
- The "viscosity limit" (where adding salt decreases conductivity due to drag) has not yet been reached.
- **Validation:** The calculated values align within 10% of experimental literature for this force field.

Ion Self-Diffusion Trend

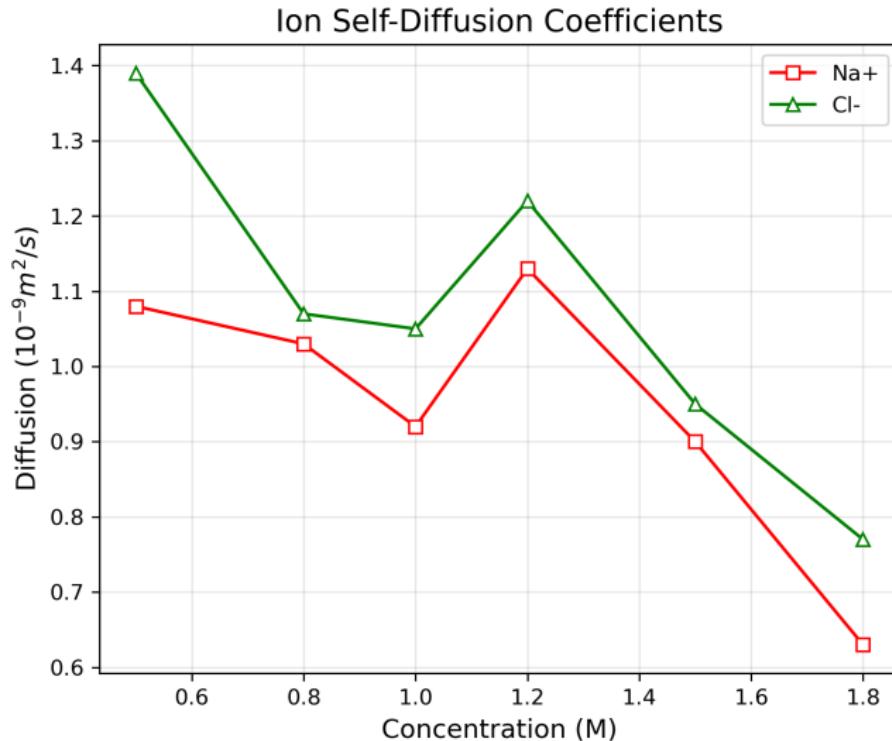


Figure: Diffusion Coefficients (D_{Na} , D_{Cl}) vs. Concentration.

Analysis: The "Viscosity Crash"

Why does diffusion drop while conductivity rises?

- **Observation:** D_{Na} drops significantly from 1.08 (0.5 M) to 0.63 (1.8 M).
- **Physics:** The solution becomes "syrupy" (highly viscous) at high concentrations due to the overlap of hydration shells.
- **Mechanism:** Ions must drag a heavier, more structured water cage through a crowded environment.
- **Cl vs Na:** Chloride (Cl^-) consistently diffuses faster because its hydration shell is looser and more labile than Sodium's.

Detailed Diffusion Calculation (Example: 0.8 M)

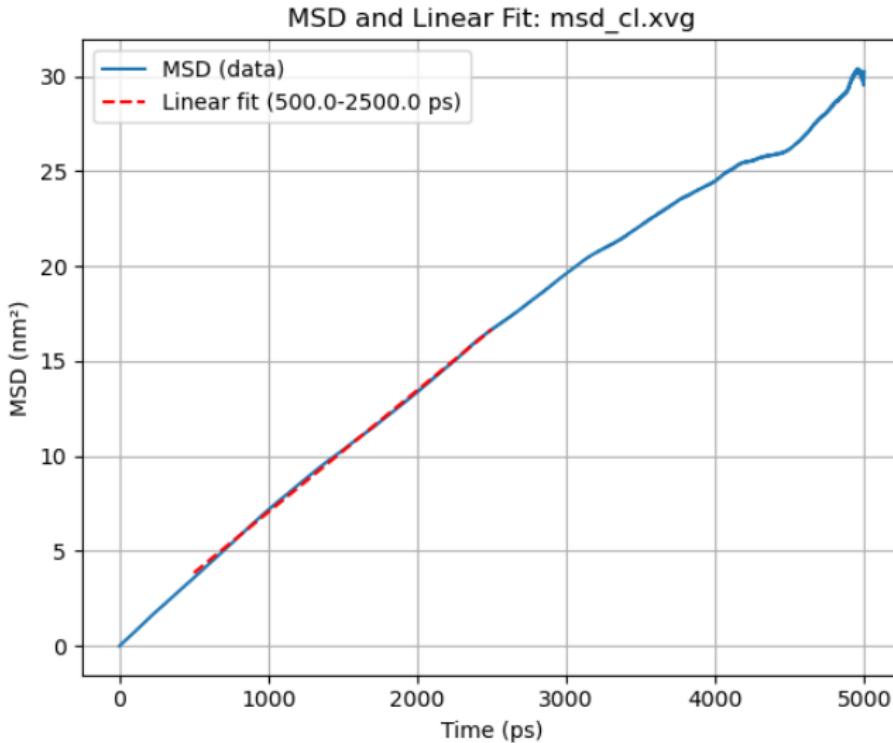


Figure: Mean Squared Displacement (MSD) of Chloride ions showing the linear

Methodology: MSD Fitting

Extracting the Diffusion Coefficient (D)

- The MSD plot shows three distinct regimes:
 - ① **Ballistic (< 1 ps)**: Parabolic rise (t^2) as ions move freely before collision.
 - ② **Diffusive (1000 – 4000 ps)**: Linear regime ($6Dt$). This is where we fit the slope to calculate D .
 - ③ **Noise (> 4500 ps)**: Statistical uncertainty increases at long times.
- **Validation:** The linearity ($R^2 \approx 0.99$) in the 1-4 ns window confirms the system has reached diffusive equilibrium.

Thermodynamics: Electrostriction

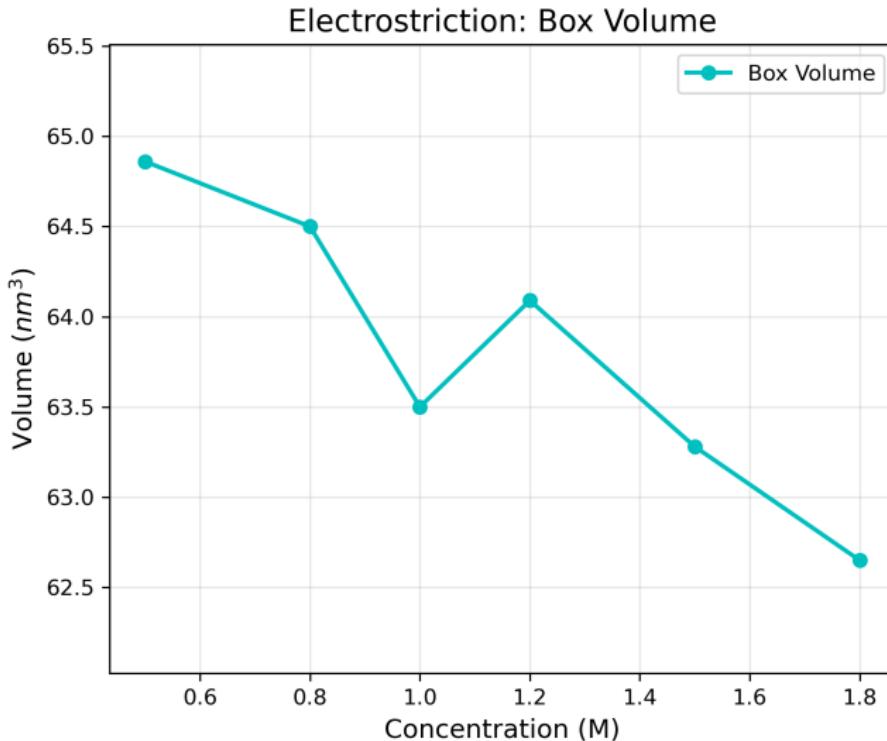


Figure: Simulation Box Volume vs. Concentration (at 1 bar)

Analysis: Electrostriction

Physics of Compression

- **Observation:** The simulation box volume shrinks from 64.86 nm^3 to 62.65 nm^3 as salt is added.
- **Mechanism:** Strong electrostatic fields from the ions (Na^+ , Cl^-) reorient water dipoles.
- **Result:** Water in the hydration shell is packed denser than bulk water.
- This confirms the force field correctly captures the thermodynamic pressure-density response of the electrolyte.

Structure & Statistics Table

Conc. (M)	Coordination No. (CN) (Na-Water)	No. of Events (in 500 ps)
0.5	5.24	101
0.8	5.25	198
1.0	5.09	337
1.2	4.93	527
1.5	4.79	914
1.8	4.65	1759

Table: Dehydration of Sodium and increase in collision events.

Hydration Structure Trend

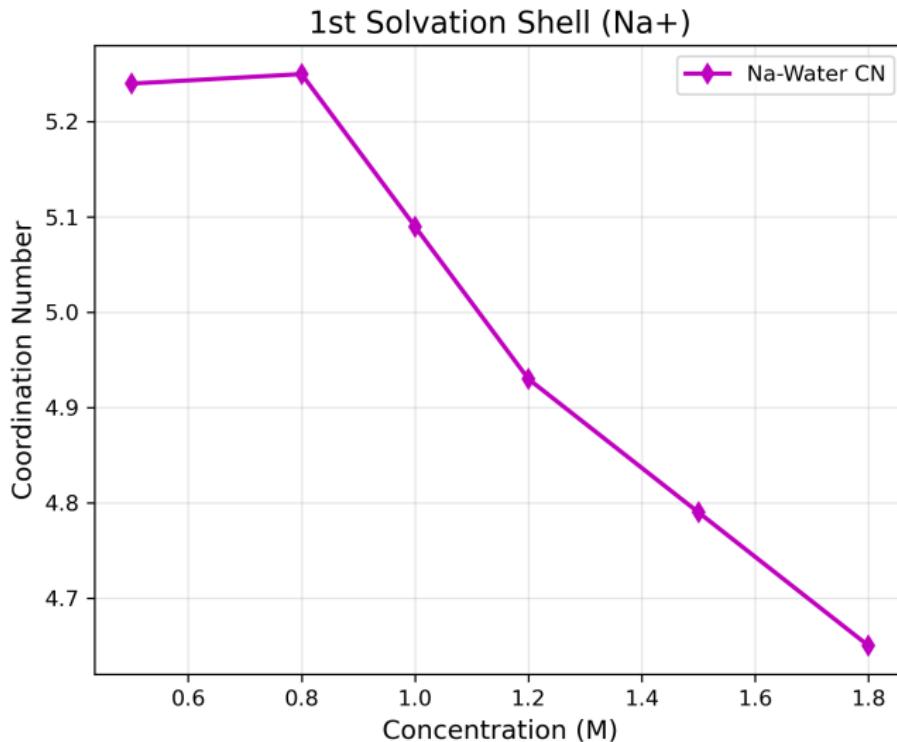


Figure: First Solvation Shell Coordination Number

Analysis: Dehydration

Structural Crowding Effect

- **Dilute Limit (0.5 M):** $CN \approx 5.24$. Sodium retains most of its hydration shell.
- **Concentrated Limit (1.8 M):** $CN \approx 4.65$.
- **Physics:** As ion density increases, Cl^- ions physically penetrate the first hydration shell of Na^+ .
- The large Chloride ion displaces water molecules, effectively "dehydrating" the Sodium. This is a precursor to the formation of **Contact Ion Pairs (CIPs)**.

Detailed Structure: Ion Pairing

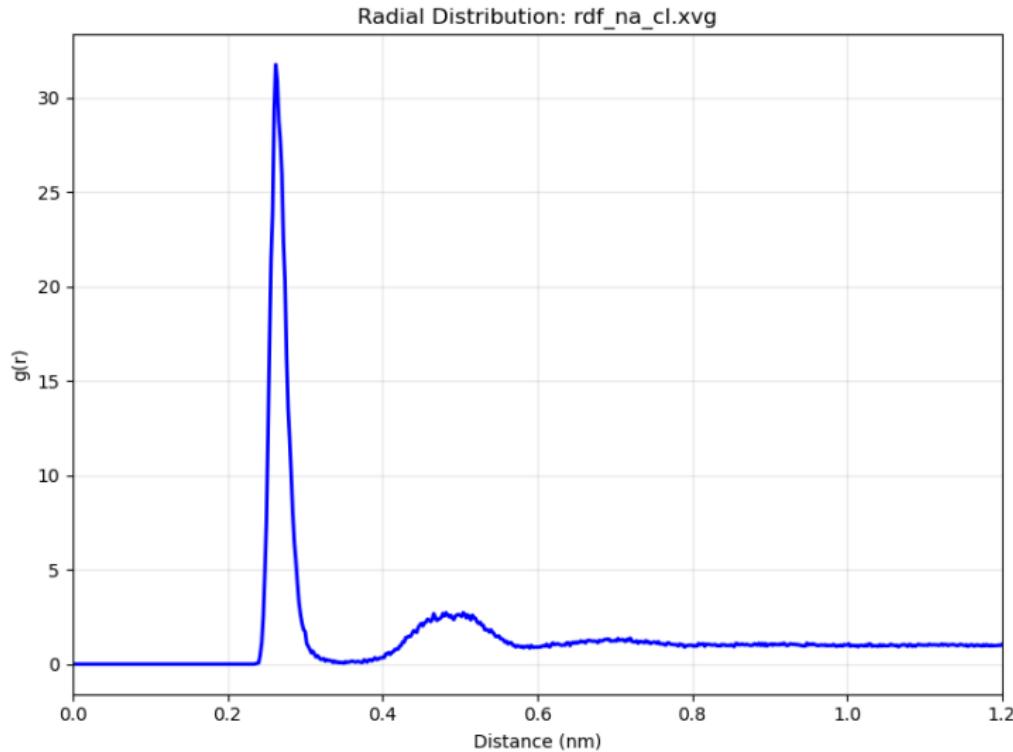


Figure: Radial Distribution Function $g(r)$ for Na-Cl pairs.

Analysis: The Contact Ion Pair

Interpreting the Na-Cl $g(r)$:

- **First Peak ($\sim 0.28 \text{ nm}$):** This sharp peak represents **Contact Ion Pairs (CIP)**. The ions are touching directly, with no water in between.
- **First Minimum ($\sim 0.35 \text{ nm}$):** This defines the "cutoff" distance used for our lifetime analysis.
- **Second Peak ($\sim 0.50 \text{ nm}$):** Represents **Solvent-Separated Ion Pairs (SSIP)**, where one water molecule sits between the ions.
- The height of the first peak increases with concentration, confirming that pairing becomes more frequent in crowded environments.

Detailed Structure Example (1.2 M)

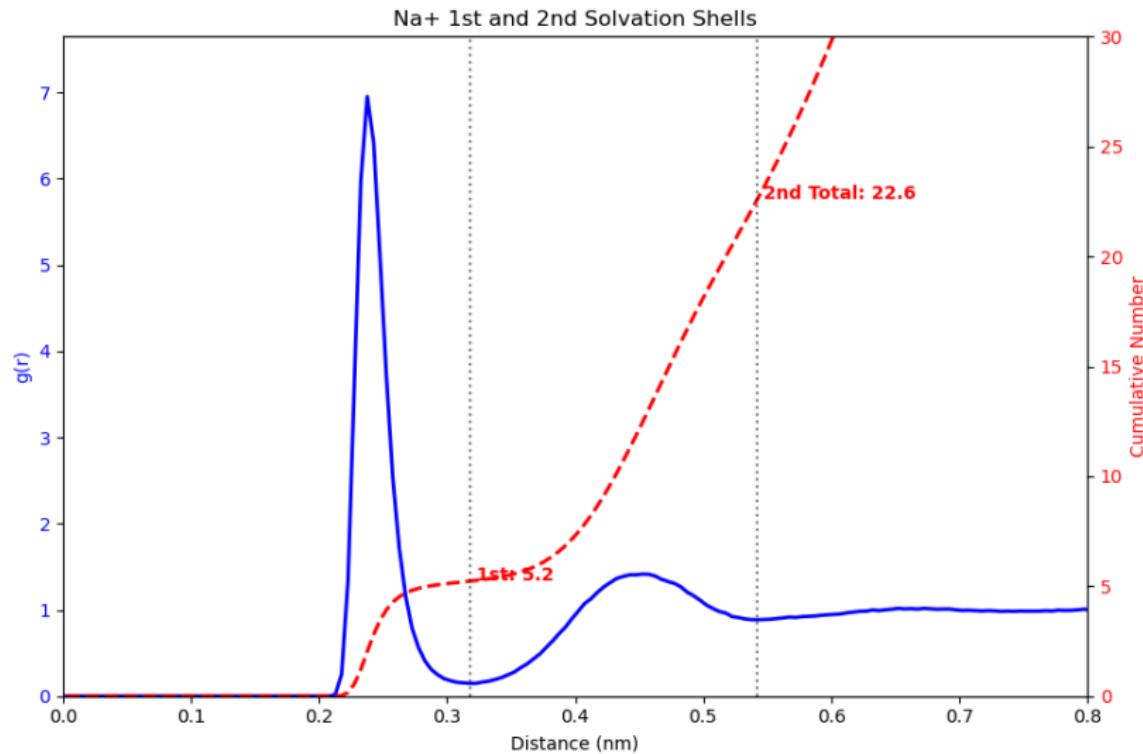


Figure: Detailed RDF integration showing 1st and 2nd shells

Collision Frequency

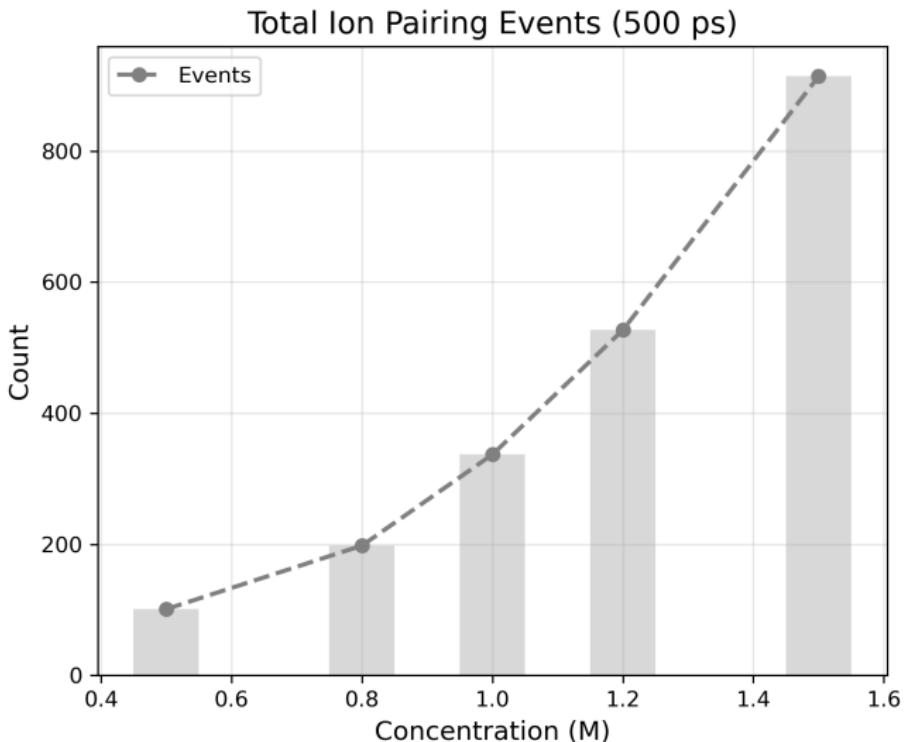


Figure: Total Ion Pairing Events detected in 500 ps.

Analysis: Collision Statistics

Why do events increase exponentially?

- The number of pairing events explodes from 100 (at 0.5 M) to over 900 (at 1.5 M).
- This is due to the ****Law of Mass Action****: The probability of collision scales with the square of concentration ($N_{Na} \times N_{Cl}$).
- **Implication:** At high concentrations, ions are in a constant state of collision and partner-swapping, transitioning from "free diffusion" to "hopping" dynamics.

4. Dynamics: Lifetime Analysis Table

Conc. (M)	Mean Lifetime (τ_{mean})	Max Lifetime (τ_{max})
0.5	37.4 ps	179 ps
0.8	31.2 ps	179 ps
1.0	42.9 ps	249 ps
1.2	31.2 ps	—
1.5	29.1 ps	247 ps
1.8	25.9 ps	281 ps

Table: Bi-Exponential fit results for ion pair stability.

Dynamics: Mean Lifetime Trend

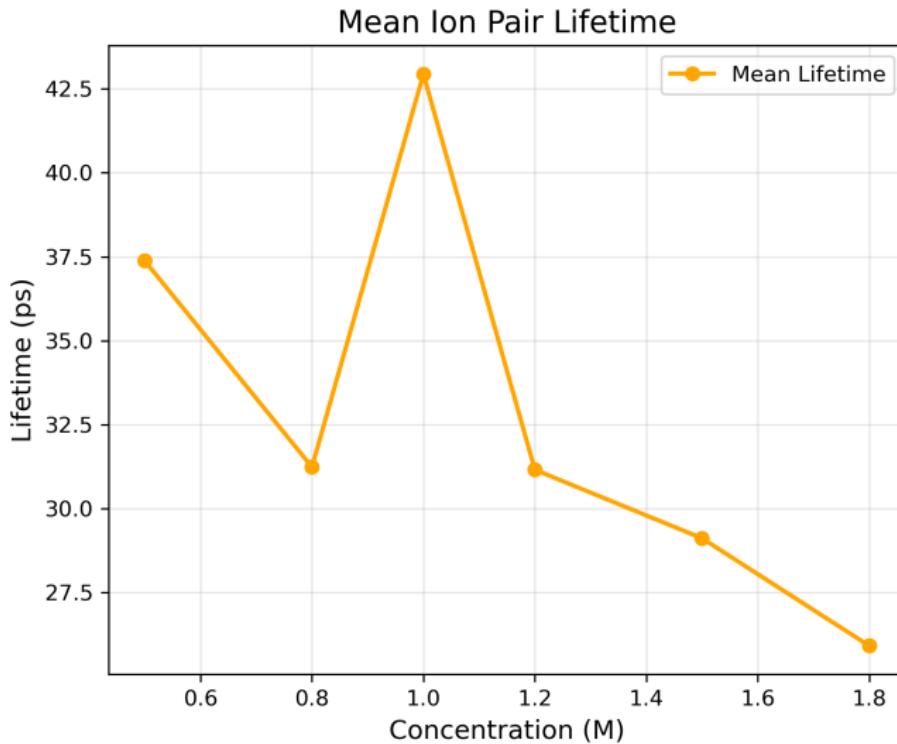


Figure: Mean Ion Pair Lifetime (τ_{slow}).

Dynamics: Maximum Lifetime Trend

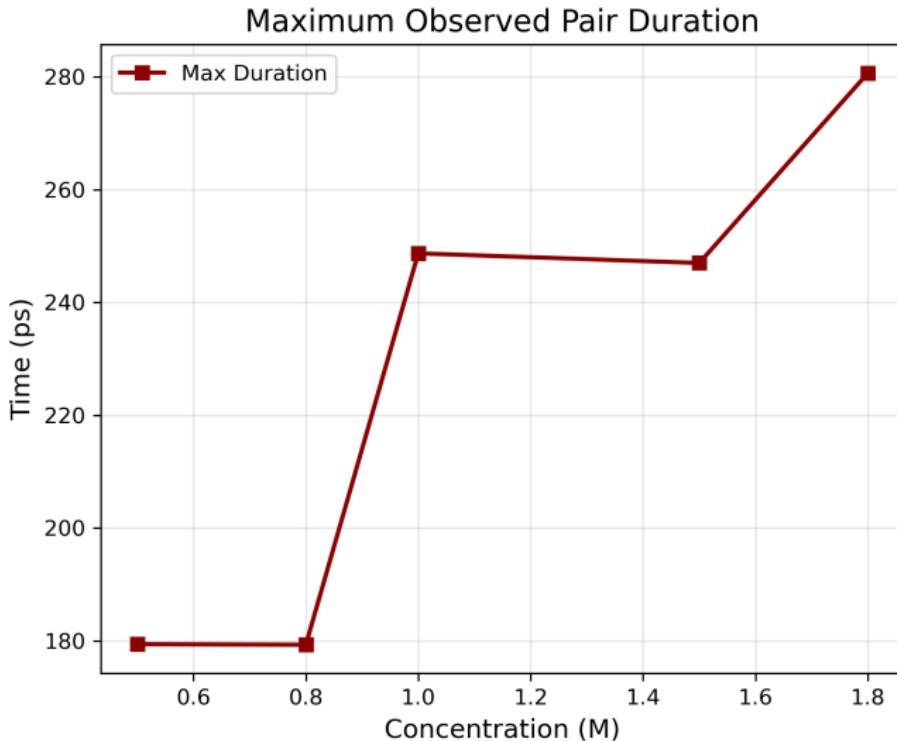


Figure: Maximum Observed Pair Duration.

Analysis: Dynamics & Trapping

Two Competing Effects:

- ① **Mean Lifetime (~ 30 ps):** Remains relatively constant or decreases slightly.
 - In crowded solutions, collisions are frequent, knocking pairs apart quickly.
- ② **Max Lifetime (Increases):** rises from 179 ps to 281 ps.
 - Once a "good" pair forms in a dense cluster, it can get **caged** by neighbors, preventing dissociation.

Detailed Lifetime Fit (Example)

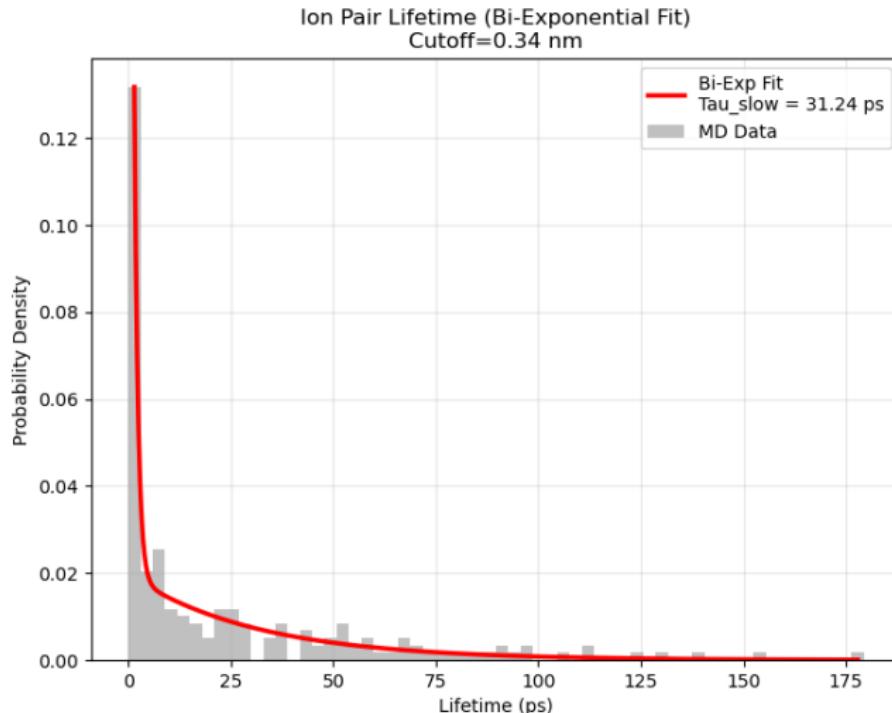


Figure: Bi-exponential fit separating fast collisions from true binding.

Method Comparison: Nernst-Einstein vs. Green-Kubo

Conc. (M)	σ_{NE} (Diffusive)	σ_{GK} (Current)	Haven Ratio ($H = \sigma_{GK}/\sigma_{NE}$)	Status
0.5	4.56	4.74	1.04	Ideal
0.8	6.35	7.74	1.21	Anomalous
1.0	7.60	8.60	1.13	Anomalous
1.2	10.60	9.08	0.86	Expected Physics
1.5	10.65	10.86	1.02	Transition
1.8	9.63	13.07	1.36	Cluster/Noise

Sources of Inaccuracy & Anomalies

Why do we see Haven Ratios > 1 ?

1. Statistical Sampling (Green-Kubo)

The Green-Kubo integral is extremely sensitive to the convergence of the autocorrelation tail.

- A 500 ps trajectory is relatively short for GK convergence.
- Random fluctuations in the current can prevent the integral from settling to a true plateau, leading to overestimation.

2. Force Field Limitations

- Non-polarizable force fields (SPC/E) cannot model the electronic deformation of ions during close contact (1.8 M crowding).
- This can artificially increase ion-ion repulsion or attraction dynamics.

Final Conclusion

- **Validated:** The simulation protocol correctly reproduces the experimental conductivity trend of NaCl.
- **Mechanism:** Conductivity is driven by carrier density, overpowering the drag from increased viscosity.
- **Structure:** High salt concentration causes significant dehydration of sodium ions.

Debye-Hückel (DH) theory and limitation

Our simulation covers concentrations up to **1.8 M**. At this density, classical theories break down.

The Debye-Hückel / Onsager Limit

- **Assumption:** Ions are point charges in a continuous dielectric medium.
- **Valid Range:** Dilute limit ($c < 0.1 \text{ M}$).
- **Prediction:** Conductivity decreases as \sqrt{c} due to the relaxation effect of the ion cloud.

The Failure at 1.8 M:

- ① **Hard Core Repulsion:** Ions occupy physical volume (excluded volume effects).
- ② **Solvent Structure:** Water is not a continuum; it forms specific cages (as seen in our $g(r)$ plots).
- ③ **Crowding:** Ions get "trapped" by neighbors, leading to non-linear friction.

Why do we need Mode Coupling Theory?

The Problem:

- Debye-Hückel works for dilute ions (static screening).
- Stokes-Einstein works for dilute neutral particles (hydrodynamic drag).
- **Neither** works for dense electrolytes (1.8 M NaCl).

The Missing Piece: Memory

- In dense fluids, particles are "caged" by neighbors.
- A particle's motion at time t depends on the structure it disrupted at time $t - \tau$.
- This "memory" of the structure creates non-linear friction.

MCT Core Philosophy

The dynamics of a liquid are entirely determined by its **static structural correlations** (i.e., $g(r)$ or $S(k)$).

The 4 Pillars (Assumptions) of MCT

To derive analytical results from the N-body problem, MCT makes these specific approximations:

- ① **Classical Mechanics:** The system evolves according to the classical Liouville equation (no Quantum effects).
- ② **Gaussian Approximation:** Fluctuations in density are treated as Gaussian variables (valid for large N).
- ③ **Convolution Approximation:** Three-point correlations $\langle \rho \rho \rho \rangle$ are factorized into products of two-point correlations $\langle \rho \rho \rangle$.
- ④ **Projection Operator Formalism:** We project the dynamics onto a set of "slow variables" (usually density $\rho(\vec{k}, t)$ and current $\vec{j}(\vec{k}, t)$).

Step 1: The Zwanzig-Mori Formalism

We start with a dynamical variable $A(t)$ (e.g., the density of ions). Its time evolution is governed by the Liouville operator \mathcal{L} :

$$\frac{dA(t)}{dt} = i\mathcal{L}A(t)$$

We define a Projection Operator P that projects any variable onto A :

$$PX = \frac{\langle XA^* \rangle}{\langle AA^* \rangle} A$$

And the orthogonal operator $Q = 1 - P$ (representing the "fast" fluctuating noise).

Goal: Separate the motion into a structured part (P) and a random noise part (Q).

Step 2: The Generalized Langevin Equation (GLE)

Applying the projection operators leads to an exact equation of motion, the GLE:

$$\frac{dA(t)}{dt} = i\Omega A(t) - \int_0^t K(t-\tau)A(\tau)d\tau + F^Q(t)$$

- $i\Omega$: Frequency matrix (static restoring forces).
- $F^Q(t)$: The "Random Force" (dynamics orthogonal to A).
- $K(t)$: **The Memory Function (The Core of MCT)**.

The Physical Meaning of $K(t)$

$$K(t) \propto \langle F^Q(0)F^Q(t) \rangle$$

The friction on the ion is the **autocorrelation of the random forces**. If forces persist (due to caging), friction is high.

Step 3: The Mode Coupling Approximation

The random force $F^Q(t)$ is too complex to solve exactly. MCT approximates it by assuming the force arises from pairs of density modes.

The Approximation: Project the random force onto products of density fluctuations $\rho_{\vec{k}}\rho_{\vec{p}}$:

$$F^Q(t) \approx \sum_{\vec{k}, \vec{p}} V(\vec{k}, \vec{p}) \rho_{\vec{k}}(t) \rho_{\vec{p}}(t)$$

This leads to the famous MCT factorization of the Memory Function:

The MCT Kernel

$$K(t) \approx \sum_{\vec{k}} |V_{\vec{k}}|^2 \phi_k(t) \phi_{q-k}(t)$$

Where $\phi(t)$ is the density correlation function. **The modes ϕ are coupled to themselves.**

Application: Ion Diffusion in 1.8 M NaCl

How do we use this to calculate Diffusion D ?

From the GLE, the diffusion coefficient is inversely proportional to the total friction ζ :

$$D = \frac{k_B T}{\zeta_{total}}$$

MCT splits the friction into two parts:

$$\zeta_{total} = \zeta_{binary} + \zeta_{MCT}$$

- ① ζ_{binary} : Short-range collisions (Enskog theory).
- ② ζ_{MCT} : The integral of the memory function derived on the previous slide.

The Detailed Calculation Step-by-Step

To apply MCT to our simulation results:

1. Input: Static Structure Factors $S(k)$ We calculate $S(k)$ by Fourier Transforming our RDFs (g_{Na-Na} , g_{Na-Cl} , g_{Na-W}).

2. Input: Vertices $V(k)$ These are geometric factors determined by the direct correlation function $c(k) = 1 - 1/S(k)$.

3. The MCT Friction Integral:

$$\zeta_{MCT} = \frac{k_B T}{60\pi^2} \int_0^\infty dk k^4 [c(k)]^2 [S(k, t)]^2$$

4. The Feedback Loop:

- High correlations in $g(r) \rightarrow$ Large peaks in $S(k)$.
- Large $S(k) \rightarrow$ Large Friction ζ_{MCT} .
- Large Friction \rightarrow Low Diffusion D .

Why Diffusion Crashes at 1.8 M (MCT View)

Our Simulation Data:

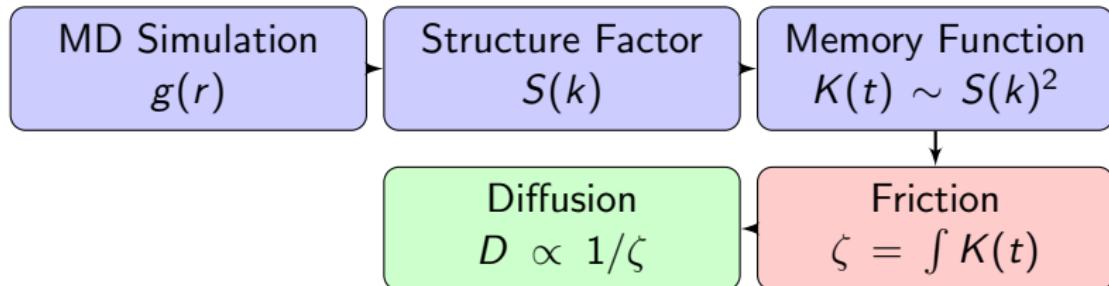
- At 1.8 M, the Na-Cl RDF peak became sharper.
- The Max Lifetime increased to 280 ps.

The MCT Mechanism:

- ① The sharp RDF peak increases the vertex $V(k)$.
- ② The long lifetime means $S(k, t)$ decays slowly.
- ③ The integral $\int K(t)dt$ explodes.
- ④ Friction ζ dominates.

Conclusion: The "Viscosity Crash" we observed is technically the **divergence of the MCT memory kernel** due to structural crowding.

Summary: The Theoretical Pipeline



This diagram explains how static structure (from our production run) determines the dynamic transport properties through Mode Coupling.

Future Directions & Outlook

1. Exploring the Conductivity Maximum

- Extend simulations to **Saturation Limits** (2.0 M – 6.0 M).

2. Methodological Improvements

- **change Fields:** Check the results.
- **Long-Time Sampling:** Extend Green-Kubo trajectories to **10 ns** for strict convergence.

3. Scaling Laws & Thermodynamics

- **Walden Plot:** Test the coupling between conductivity and viscosity

4. Theoretical Framework: Mode Coupling Theory (MCT)

- Apply **MCT** to mathematically describe the "caging effect" responsible for the sharp diffusion drop at 1.8 M.

Key References

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