

# Ionic Conductivity & Solvation Dynamics of NaCl

## A Molecular Dynamics Study (0.5 M – 1.8 M)

Debanjan Sinha Mahapatra

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# Simulation Details (1.0 M Run)

Parameter	Value / Notes
Software	GROMACS 2024.5
System	39 Na <sup>+</sup> , 39 Cl <sup>-</sup> , 2084 Water (1.0 M)
Box	≈ 4 nm cubic box
Force fields	<b>GROMOS 54A7</b> (Ions), <b>SPC/E</b> (Water)
Ensemble	NVT (100 ps) → NPT (100 ps) Equil. <b>NPT Production</b> (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)
<b>GK Analysis</b>	gmx current (from 10 fs .trr file)
<b>NE Analysis</b>	gmx msd (from unwrapped .xtc)
<b>Structure</b>	gmx rdf, gmx select -olt

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

# Methodology: Green-Kubo Conductivity

- 1. The Theory** Electrical conductivity ( $\sigma$ ) 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.

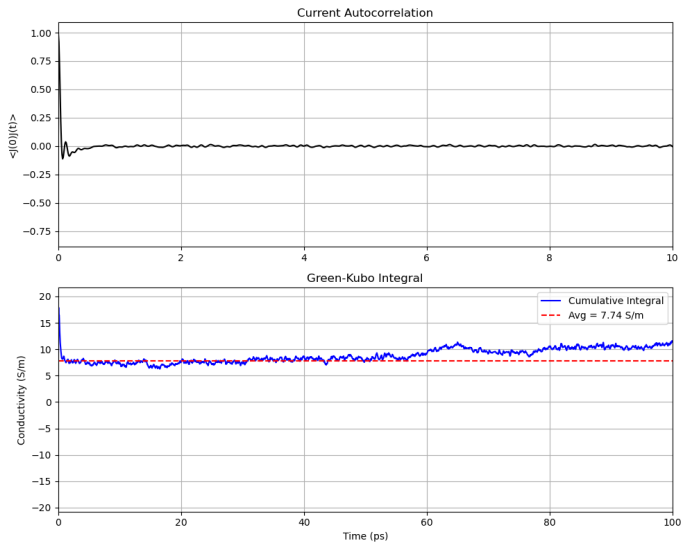


Figure: Current ACF and Conductivity Integral.

## 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  $\sigma_{GK}$ .

# 1. Electrical Conductivity Data

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

Concentration (M)	Simulated $\sigma_{GK}$ (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

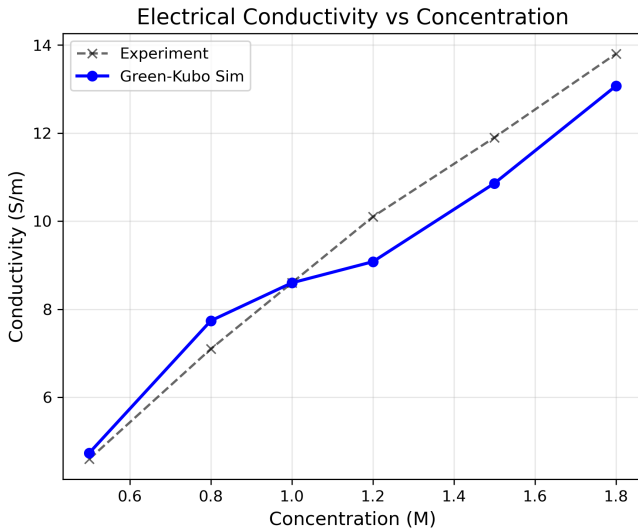


Figure: Green-Kubo Conductivity vs. Concentration.

## 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

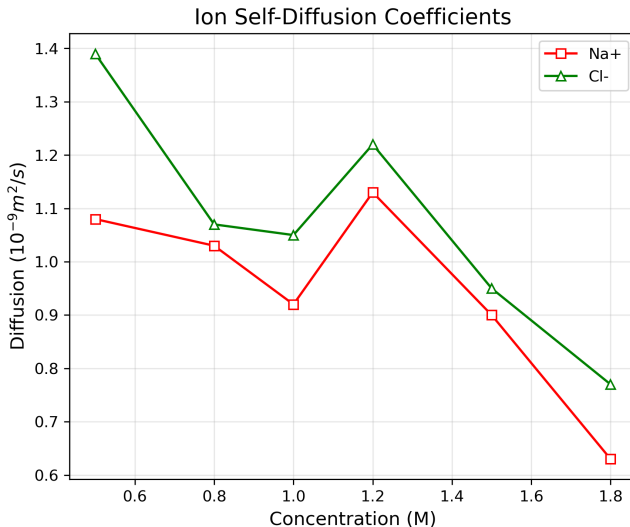


Figure: Diffusion Coefficients ( $D_{Na}$ ,  $D_{Cl}$ ) vs. Concentration.

# 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)

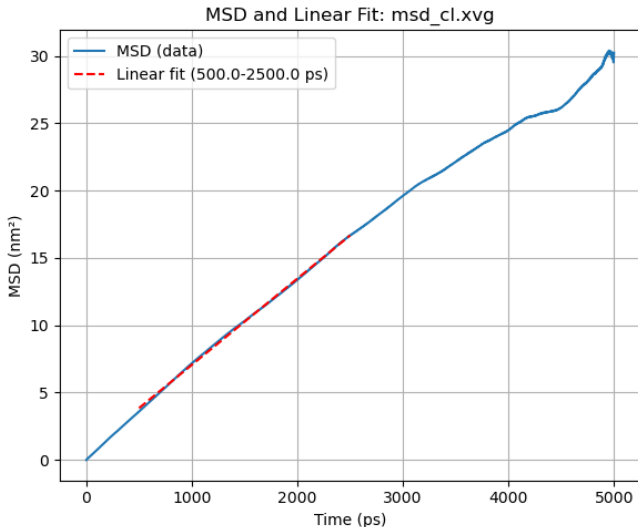


Figure: Mean Squared Displacement (MSD) of Chloride ions showing the linear

## 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

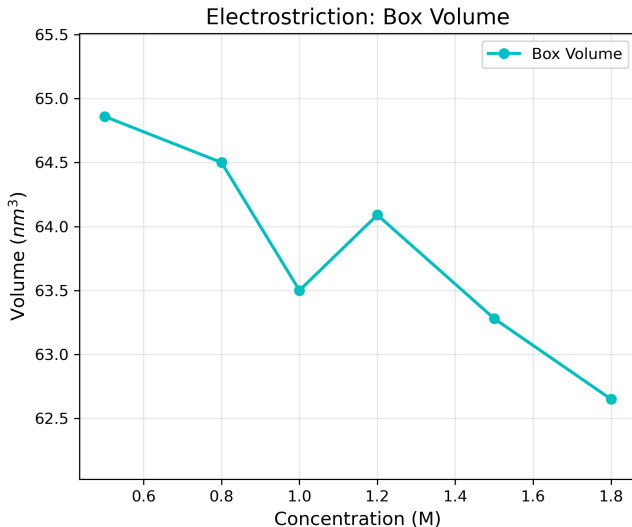


Figure: Simulation Box Volume vs. Concentration (at 1 bar)

## Physics of Compression

- **Observation:** The simulation box volume shrinks from  $64.86 \text{ nm}^3$  to  $62.65 \text{ nm}^3$  as salt is added.
- **Mechanism:** Strong electrostatic fields from the ions ( $\text{Na}^+$ ,  $\text{Cl}^-$ ) 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

<b>Conc. (M)</b>	<b>Coordination No. (CN) (Na-Water)</b>	<b>No. of Events (in 500 ps)</b>
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

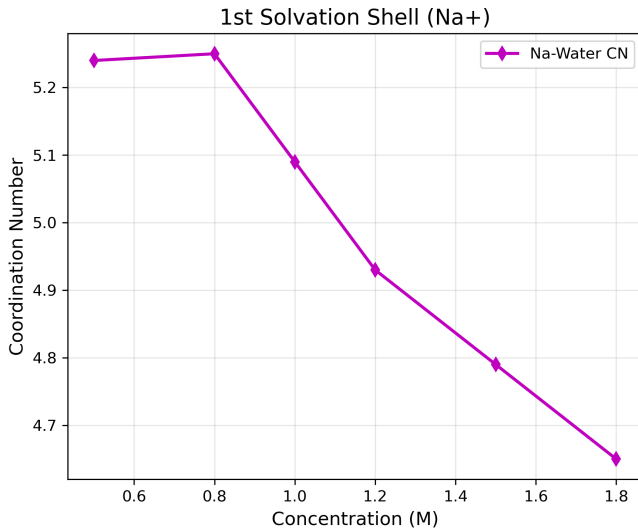


Figure: First Solvation Shell Coordination Number



## 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,  $\text{Cl}^-$  ions physically penetrate the first hydration shell of  $\text{Na}^+$ .
- 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

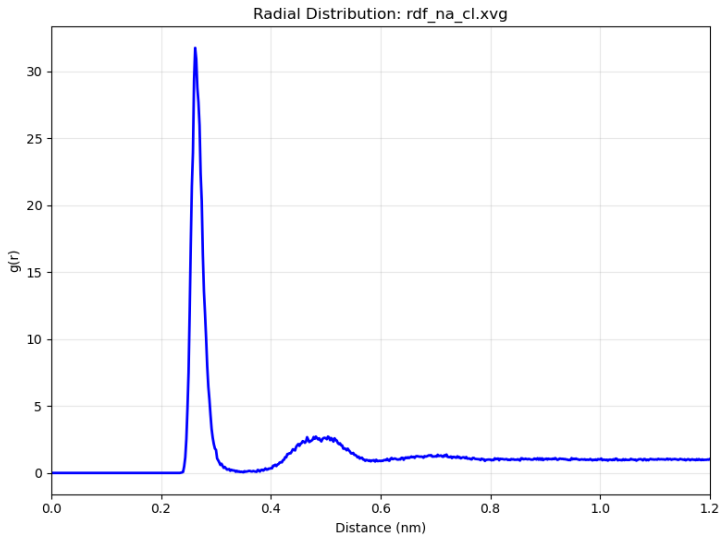


Figure: Radial Distribution Function  $g(r)$  for Na-Cl pairs.

# Analysis: The Contact Ion Pair

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

- **First Peak ( $\sim 0.28$  nm):** This sharp peak represents **\*\*Contact Ion Pairs (CIP)\*\***. The ions are touching directly, with no water in between.
- **First Minimum ( $\sim 0.35$  nm):** This defines the "cutoff" distance used for our lifetime analysis.
- **Second Peak ( $\sim 0.50$  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)

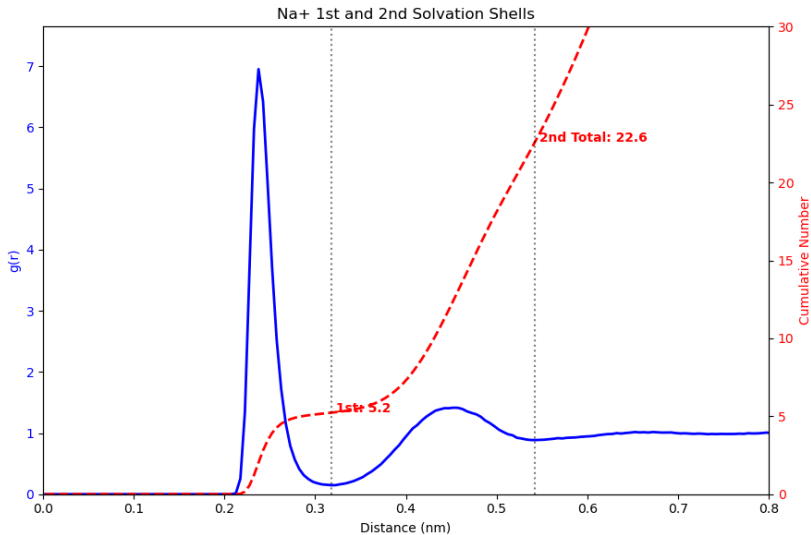


Figure: Detailed RDF integration showing 1st and 2nd shells.

# Collision Frequency

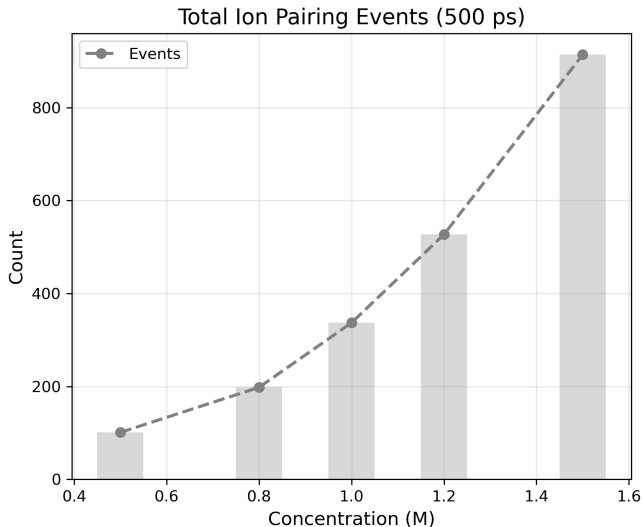


Figure: Total Ion Pairing Events detected in 500 ps.

## 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 ( $\tau_{mean}$ )	Max Lifetime ( $\tau_{max}$ )
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

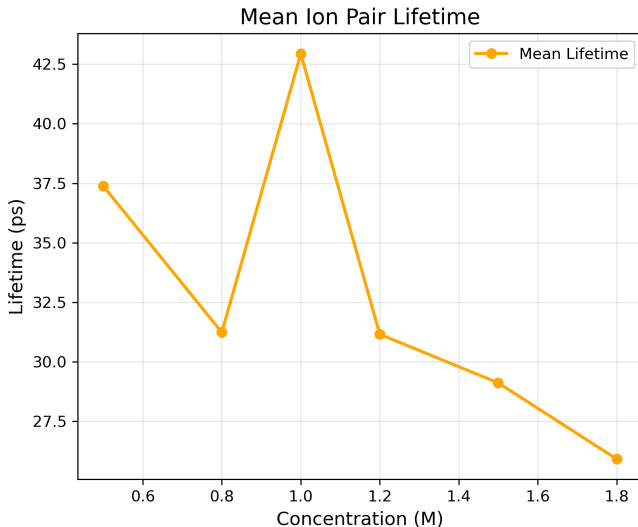


Figure: Mean Ion Pair Lifetime ( $\tau_{slow}$ ).



# Dynamics: Maximum Lifetime Trend

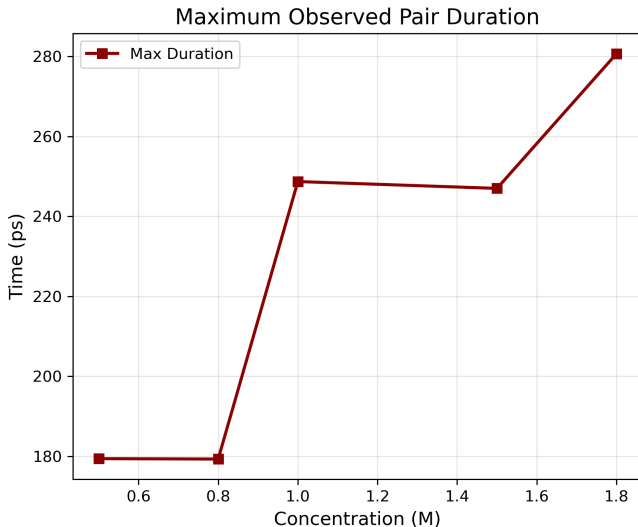


Figure: Maximum Observed Pair Duration.

## Two Competing Effects:

- ① **Mean Lifetime ( $\sim 30$  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)

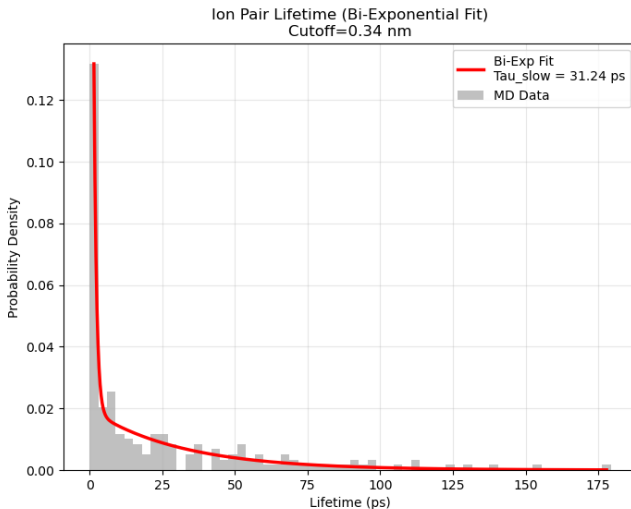


Figure: Bi-exponential fit separating fast collisions from true binding.

# Method Comparison: Nernst-Einstein vs. Green-Kubo

Conc. (M)	$\sigma_{NE}$ (Diffusive)	$\sigma_{GK}$ (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
<b>1.2</b>	<b>10.60</b>	<b>9.08</b>	<b>0.86</b>	<b>Expected Physics</b>
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.

- **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 ( $c < 0.1$  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  $\phi$  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  $\zeta$ :

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

MCT splits the friction into two parts:

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

- 1  $\zeta_{binary}$ : Short-range collisions (Enskog theory).
- 2  $\zeta_{MCT}$ : 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  $\zeta_{MCT}$ .
- Large Friction  $\rightarrow$  Low Diffusion  $D$ .

# Why Diffusion Crashes at 1.8 M (MCT View)

## Our Simulation Data:

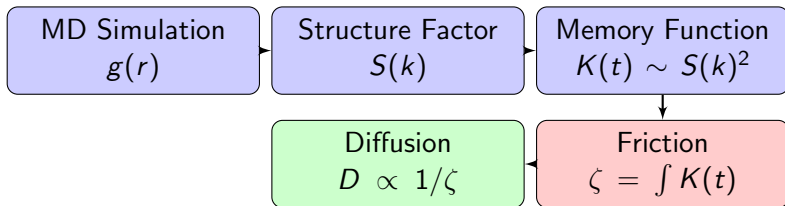
- At 1.8 M, the Na-Cl RDF peak became sharper.
- The Max Lifetime increased to 280 ps.

## 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  $\zeta$  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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