

Entropy Scaling of Viscosity for Molecular Models of Molten Salts

Jeffrey M. Young,^{1, a)} Ian H. Bell,^{1, b)} and Allan H. Harvey^{1, c)}

Applied Chemicals and Materials Division, National Institute of Standards and Technology, Boulder, CO 80305, USA

(Dated: 30 November 2022)

Entropy scaling relates dynamic and thermodynamic properties by reducing the viscosity to a function of only the residual entropy. Molecular simulations are used to investigate the entropy scaling of the viscosity of three models of sodium chloride and five monovalent salts. Even though the correlation between the potential energy and the virial is weak, entropy scaling applies at liquid densities for all models and salts investigated. At lower densities, entropy scaling breaks down due to the formation of ion pairs and chains. Entropy scaling can be used to develop more extendable correlations for the dynamic properties of molten salts.

Contribution of the National Institute of Standards and Technology, not subject to copyright in the United States.

^{a)}Present Address: Carbon America, Arvada, CO 80002, USA

^{b)}Electronic mail: ian.bell@nist.gov

^{c)}Electronic mail: allan.harvey@nist.gov

I. INTRODUCTION

Molten salts are found in many energy applications. They can be used as the electrolyte in fuel cells or batteries^{1,2}, as well as for transporting and storing heat for nuclear reactors³ and solar power.⁴ The development of widely applicable models for properties such as the viscosity of molten salts is essential for designing equipment and processes. However, experimental studies of molten salts are challenging and expensive due to their high melting temperatures, so there is only limited experimental data over a small range of conditions.

One way to improve thermophysical property correlations is to improve their theoretical basis. Entropy scaling is a method that allows this, relating dynamic and thermodynamic properties. Entropy scaling states that when dynamic properties, such as viscosity, are reduced to a dimensionless form as will be explained below, they become only a function of the residual entropy (the difference between the entropy and that of an ideal gas).⁵ This not only relates the dynamic viscosity to the thermodynamic entropy but also reduces the dimensionality of the data. Viscosity, which is normally a two-dimensional function of temperature and density (or pressure) becomes a one-dimensional function, which is much simpler to fit.⁶ However, entropy scaling is not an exact relationship for real fluids. For a fluid interacting with an inverse power-law pair potential ($\frac{1}{r^n}$ where r is the distance between interacting atoms and $n > 0$), entropy scaling is exact for any state.⁷ But for real fluids, or even fluid models with interactions more complex than inverse power-law repulsion, entropy scaling is only approximate.

The theory behind entropy scaling is based on the idea that a fluid has curves in state space where the reduced structure is constant, along which properties such as residual entropy and reduced viscosity are also constant.⁸ The presence of these isomorphs can be detected by a correlation between the potential energy U and the virial of the forces W . The virial is defined as

$$W = -\frac{1}{3} \sum_i \mathbf{r}_i \cdot \nabla_{\mathbf{r}_i} U, \quad (1)$$

where $\mathbf{r}_i$ is the position of particle i . The correlation between U and W is measured by the Roskilde correlation coefficient,⁷ R_{Ros} (also called the R -value), where

$$R_{\text{Ros}} = \frac{\langle \Delta U \Delta W \rangle}{\sqrt{\langle (\Delta U)^2 \rangle \langle (\Delta W)^2 \rangle}}. \quad (2)$$

Here $\langle \rangle$ indicates an NVT ensemble average, and Δ indicates the deviation of the potential energy and virial from the average. A system with a strong correlation ($R_{\text{Ros}} \approx 1$) will have isomorphs and should follow entropy scaling.^{8,9}

Length, energy and time scales are needed to nondimensionalize dynamic properties into their reduced forms. The relevant length scale l of the system is the distance between molecules, or

$$l = \left(\frac{V}{N} \right)^{1/3} = \rho_N^{-1/3}, \quad (3)$$

where N is the number of molecules and ρ_N is the number density. The energy scale ε is the thermal energy,

$$\varepsilon = k_B T, \quad (4)$$

where k_B is the Boltzmann constant and T is the absolute temperature. The characteristic timescale t is therefore

$$t = \frac{l}{\sqrt{\varepsilon/m}}, \quad (5)$$

where m is the mass of one molecule. Reducing the viscosity η by these dimensions gives

$$\tilde{\eta} = \eta \frac{l^3}{\varepsilon t} = \frac{\eta}{\rho_N^{2/3} \sqrt{m k_B T}}. \quad (6)$$

As the density goes to zero, the reduced viscosity $\tilde{\eta}$ diverges since the viscosity approaches the finite kinetic theory value while the $\rho_N^{2/3}$ in the denominator of eq. 6 approaches zero. A second-order virial expansion shows that the residual entropy, s^r , is proportional to the density.¹⁰ Therefore, as the density goes to zero, the residual entropy approaches zero at the same rate, and the divergence of the reduced viscosity can be removed by multiplying eq. 6 by $(-s^r/k_B)^{2/3}$, and defining the modified scaled viscosity as η^+ ,¹⁰ where

$$\eta^+ = \frac{\eta}{\rho_N^{2/3} \sqrt{m k_B T}} \left(-\frac{s^r}{k_B} \right)^{2/3}. \quad (7)$$

In this work, the residual entropy is defined as the difference in entropy between a real fluid and an ideal gas at the same density, ρ , and temperature:

$$s^r(\rho, T) = s(\rho, T) - s^{\text{IG}}(\rho, T). \quad (8)$$

To simplify notation, the nondimensional residual entropy is defined as

$$s^+ = -\frac{s^r}{k_B}. \quad (9)$$

Entropy scaling of molten salts has been studied previously. The Chakravarty group has investigated the entropy scaling of ionic melts such as SiO_2 and BeF_2 with molecular dynamics simulations.^{11–14} They found that entropy scaling showed some scatter, but generally worked for these systems. However, they used a pair correlation approximation to calculate the entropy. Recently, Knudsen et al. studied a molten salt model at supercritical temperatures and high densities using molecular dynamics simulations.¹⁵ They found that R_{Ros} ranged from 0.7 to 0.95, and that entropy scaling held true even for the low R_{Ros} conditions. However, they did not investigate the lower temperature conditions where Coulomb interactions play a larger role. The Maginn group has calculated the viscosity of a number of monovalent molten salts using both fixed-charge and polarizable models.¹⁶ Additionally, Young and O’Connell found that experimental reduced transport properties of monovalent salts depend only on a reduced temperature calculated from the thermal expansivity.¹⁷

In this work, molecular simulations are used to investigate the entropy scaling behavior of molten monovalent molten salts. Three models are used for NaCl, and the best-performing model was used to investigate the effect of changing the cation and anion of the salt on the entropy scaling behavior.

II. MODELS

A number of molecular models were used for NaCl and other monovalent salts. For molten NaCl, three models were investigated. These models are the rigid-ion model (RIM),^{16,18,19} the Joung-Cheatham model for ions in SPC/E water (JC),²⁰ and the Madrid model.²¹ All three of these are non-polarizable, fixed-charge models. However, they differ in the fitting targets and the functional form. As seen in Table I, the RIM model is parameterized from solid salt properties such as ultraviolet absorbance¹⁸ and thermal expansivity¹⁹. The model uses the Born-Mayer-Huggins (BMH) potential for the repulsion and induced dipole and quadrupole attractions. The form of the BMH potential is

$$U(r) = A \exp\left(\frac{\sigma - r}{B}\right) - \frac{C}{r^6} - \frac{D}{r^8}. \quad (10)$$

Here, U is the non-Coulombic potential energy between two ions, r is the distance between two ions, and σ , A , B , C , and D are the model parameters. The RIM model uses full charges on the ions. This means that the Na^+ ion has a charge of +1, and the Cl^- ion has

TABLE I. NaCl models investigated

Model	Fitting target	Functional form
RIM ^{18,19}	Solid properties	BMH + Full charges
JC ²⁰	Aqueous solution and solid	LJ + Full charges
Madrid ²¹	Aqueous solution and solid	LJ + Scaled charges

a charge of -1.

The JC model for NaCl is fit to aqueous solution and solid salt properties. These are the hydration free energy, the ion-water radial distribution function, and the salt crystal lattice constants and energy. The JC model uses Lennard-Jones (LJ) interactions to describe the repulsion and dispersion attraction as well as full charges on the ions. The LJ potential is

$$U(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right], \quad (11)$$

where ϵ and σ are the model parameters.

The Madrid model is also fit to aqueous solution and solid properties: the activity coefficients, solution and solid density, and the free energy difference between the solution and solid. Unlike the other models, the Madrid model uses scaled charges on the ions. This means that the charge on the Na^+ ion is 0.85 and on the Cl^- ion is -0.85 . The Madrid model uses the LJ potential for the repulsion and dispersion interactions. Parameters for all of the investigated models are given in Tables S1 and S2 in the Supplementary Material.

The scaled charges on the Madrid model account for the missing polarizability. In a simulation of an aqueous system, the dielectric constant of the water model is often lower than that of real water. For example, SPC/E water has a dielectric constant of 73 at 298.15 K and 1 bar²² as compared to 78.4 of real water.²³ To obtain the apparent interactions between ions in such a system, the charges must be scaled by the difference between the dielectric constant of the water model and that of real water. The deficiency of many nonpolarizable water models in predicting the dielectric constant of water is partly due to their inability to represent the electronic contribution to the dielectric constant.²⁴ This electronic (or high-frequency) contribution is around 2,²⁵ on the order of magnitude of the difference between SPC/E water and real water. In a molten salt system there is no water; however, a nonpolarizable molten salt model will still fail to represent the electronic contribution to the dielectric constant of the molten salt. This can also be thought of

as charge transfer between ions. A recent ab-initio molecular dynamics study has found charges between ± 0.84 and ± 0.9 on molten alkali halide salts.²⁶ Therefore, the charges of ± 0.85 on the Madrid model are still reasonable for a molten salt system. It has been found that scaled charge models generally have faster (and often more accurate) dynamics but are worse at predicting thermodynamic properties when compared to nonpolarizable full charge models.^{27–29}

The RIM models for LiCl, KCl, NaBr, and NaI were also investigated.^{18,19} These models use the same functional form and were fit to the same targets as the NaCl RIM model. The parameters are given in Table S2 in the Supplementary Material.

III. METHODS

Molecular dynamics simulations were used to calculate the entropy and viscosity of the molten salts with the LAMMPS package.³⁰ These simulations permit the investigation of properties over a large temperature and pressure range. In addition, both the viscosity and entropy can be directly calculated from simulations. The chosen temperatures were 1200, 1500, 1800, 2100, and 2500 K, and the chosen pressures were 0.1, 500, and 1000 MPa. At 0.1 MPa, the Madrid model was only simulated up to 1800 K since higher temperatures begin to approach the model’s vapor-liquid coexistence curve.²⁹

The viscosities of the molten salts were determined using the Green-Kubo method.³¹ This method uses the autocorrelation of the pressure tensor to determine the viscosity,

$$\eta = \frac{V}{10k_{\text{B}}T} \int_0^\infty \mathbf{P}(0) : \mathbf{P}(t) dt. \quad (12)$$

The pressure tensor $\mathbf{P}$ was stored at every simulation timestep to capture the short-time behavior of the correlation functions. Autocorrelation functions of the pressure tensor were calculated from each simulation with 0.5 ps of separation between starting points. The average of the autocorrelation functions was taken and then integrated as in Eq. 12. For most simulations, the integral in Eq. 12 converged by 3 ps, so the viscosity was taken as the average value of the integral with an upper limit between 3-5 ps. For the JC model at 1200 K and 1000 MPa, the viscosity only converged after 5 ps. In this case, the integral in Eq. 12 was computed up to 7 ps, and the average viscosity was taken from the region between 5-7 ps.

The entropy of the molten salts was determined from the chemical potential. The definition of chemical potential, μ , is the change in free energy $\mathcal{F}$ with the number of molecules,

$$\mu = \frac{\partial \mathcal{F}}{\partial N}. \quad (13)$$

If $\mathcal{F}$ is the Gibbs free energy the pressure and temperature are held constant for the derivative in Eq. 13, and if $\mathcal{F}$ is the Helmholtz free energy the volume and temperature are held constant. Approximating Eq. 13 as a finite difference, the chemical potential becomes the free energy change of inserting one molecule (or ion pair) into the melt:

$$\mu \approx \mathcal{F}(N+1) - \mathcal{F}(N). \quad (14)$$

The residual chemical potential and residual free energy change are likewise related:

$$\mu^r \approx \mathcal{F}^r(N+1) - \mathcal{F}^r(N). \quad (15)$$

This residual free energy change was determined using the multistate Bennett acceptance ratio (MBAR) method and thermodynamic integration.³² For the JC and Madrid models, the residual chemical potentials along the three isobars were taken from Ref. 29.

Since molten salts have strong interactions between ions, the ion pairs had to be inserted gradually. The dispersion and repulsion interactions were turned on first, followed by the Coulomb interactions. For the JC and Madrid models, 11 stages were used to scale the Lennard-Jones interactions and 21 stages for the Coulomb interactions. Soft core interactions were used for the LJ interactions to avoid adding a discontinuity at $r = 0$. This soft core potential is

$$U_\lambda = \lambda_{\text{LJ}}^2 4\epsilon \left(\frac{1}{\left[0.5(1 - \lambda_{\text{LJ}})^2 + \left(\frac{r}{\sigma}\right)^6\right]^2} - \frac{1}{0.5(1 - \lambda_{\text{LJ}})^2 + \left(\frac{r}{\sigma}\right)^6} \right), \quad (16)$$

where the insertion stages are $\lambda_{\text{LJ}} = 0, 0.1, \dots, 1$ and ϵ and σ are the parameters for the LJ interaction. The Coulomb interactions were added by scaling the charges on the ions, q , as

$$q_\lambda = q\sqrt{\lambda_q} \quad (17)$$

with $\lambda_q = 0, 0.05, \dots, 1$.

For the RIM models, 16 stages were used to turn on the BMH interactions. The repulsive component was added first by scaling the parameter A in Eq. 10 exponentially as

$$A_\lambda = A \frac{e^{10\lambda_A} - 1}{e^{10} - 1} \quad (18)$$

with $\lambda_A = 0, 0.1, \dots, 1$. The attractive C and D parameters were then added by linearly scaling them in 6 stages. As for the JC and Madrid models, the Coulomb interactions were added in 21 stages. The total residual chemical potential is the sum of the free energy changes between each insertion stage.

For the isobars, the chemical potential was determined using MBAR at the lowest temperature of 1200 K and then thermodynamic integration along the isobar was used to calculate the chemical potential at the higher temperatures. The residual chemical potential difference between temperatures T_1 and T_2 at constant pressure P is

$$\frac{\mu^r(T_2, P)}{RT_2} - \frac{\mu^r(T_1, P)}{RT_1} = - \int_{T_1}^{T_2} \frac{h^r(T)}{RT^2} dT - \ln \frac{T_2 v_1}{T_1 v_2}, \quad (19)$$

where $h^r(T)$ is the molar residual enthalpy at each T , and v_1 and v_2 are the molar volumes at T_1 and T_2 respectively. The integral was calculated using 5-point Gauss-Legendre quadrature between each temperature of 1200, 1500, 1800, 2100, and 2500 K.

The residual entropy is related to the residual chemical potential by

$$s^r = \frac{h^r - \mu^r}{T}, \quad (20)$$

where the residual enthalpy is calculated from the residual internal energy, u^r , as

$$h^r = u^r + P^r v. \quad (21)$$

The residual internal energy is equal to the potential energy of the interactions in the molecular simulations. The residual pressure is

$$P^r = P - \frac{2RT}{v}, \quad (22)$$

where the factor 2 is present because there are two separate ions in each monovalent salt molecule.

The experimental residual entropy is calculated from the values in the NIST-JANAF tables³³ for the ideal gas ions and liquid salt. Since the residual entropy involves comparing to the ideal gas at the same density rather than at the same pressure, the ideal gas entropy must be corrected from the NIST-JANAF reference state of 1 bar to the ideal gas entropy at the experimental density. The residual entropy is therefore

$$s^r = s_{+-} - \left[s_+^\circ + s_-^\circ + 2R \ln \left(\frac{P^\circ}{\rho RT} \right) \right]. \quad (23)$$

Here, s_{+-} is the entropy of the molten salt, s_+° is the entropy of the ideal gas cation, and s_-° is the entropy of the ideal gas anion (all taken from the NIST-JANAF tables at temperature T). P° is the reference pressure of s_+° and s_-° , and is set to 0.1 MPa in the NIST-JANAF tables. In Eq. 23, the ideal gas entropy of mixing $2R \ln(1/2)$ cancels with the $2P^\circ$ obtained from adding the cation and anion partial pressures. The density in Eq. 23 is the density of the molten salt at T and P and is taken from Ref. 34.

Values of R_{Ros} are calculated from Eq. 2 using NVT simulations at each temperature at the density of the 1200 K, 0.1 MPa state point. The heat capacities are calculated using the procedure in Ref. 35. For all the molecular simulations, the timestep was set to 1 fs. The real-space cutoff was set to 1 nm except for the very low density simulations which used cutoffs up to 5 nm. The particle-particle particle-mesh method was used to account for the long-range Coulomb interactions, and standard long-range corrections were used for the dispersion interactions. The viscosity was calculated from a 10 ns simulation in the NVE ensemble after equilibrating the system to the correct pressure and temperature in the NPT and NVT ensembles. The MBAR and thermodynamic integration simulations were run for 5 ns in the NPT or NVT ensembles (depending on whether the simulation was for a fixed pressure or density point) using a Nose-Hoover thermostat and barostat. To estimate the uncertainty of all quantities, five independent simulations were run for each calculation. The uncertainties are reported in the supplementary material as twice the standard error in the mean.

IV. RESULTS

The residual entropy and viscosity of the three NaCl models at 0.1 MPa are compared to experimental results in Figures 1 and 2. The experimental entropy was taken from the NIST-JANAF thermochemical tables³³ and is extrapolated past 1500 K assuming the heat capacity is constant at the 1500 K value. The uncertainty in the experimental entropy is expected to be less than 1 J·mol⁻¹·K⁻¹.³³ Experimental viscosity fitted to the form of an Arrhenius equation was taken from Tasidou et al.³⁶ The uncertainty in this correlation is 2.4 %, and it is extrapolated past its upper limit of 1249 K.

The simulations all predict a more negative residual entropy than experiments, with the Madrid and RIM models predicting similar values closer to experiments than the JC model.

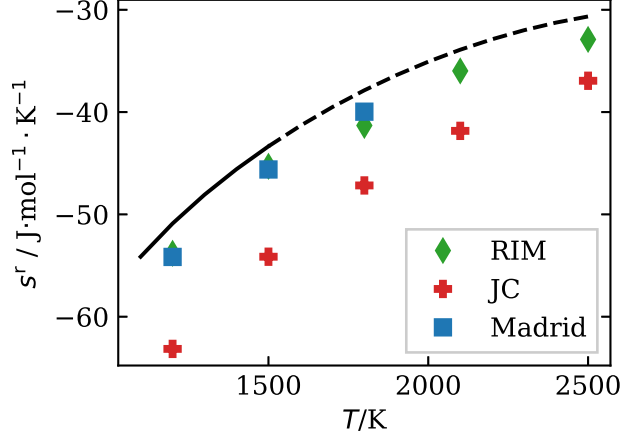


FIG. 1. Residual entropy of three NaCl models at 0.1 MPa. Uncertainties are comparable to the size of the symbols. The solid curve represents the experimental values,³³ and the dashed curve is the extrapolation to higher temperatures.

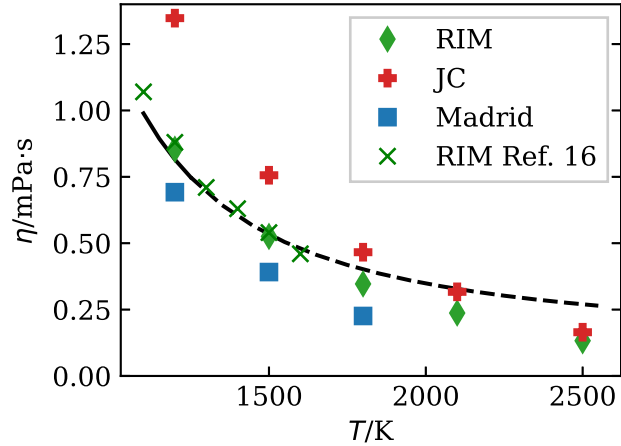


FIG. 2. Viscosity of three NaCl models at 0.1 MPa. Uncertainties are comparable to the size of the symbols. The solid curve represents the correlation fitted to experiment,³⁶ and the dashed curve is the extrapolation of the correlation to higher temperatures. Literature data from Ref. 16 for the RIM NaCl model is also shown.

The good performance of the scaled charge Madrid model for the residual entropy means that an inaccurate enthalpy is the main cause of the inaccurate chemical potential seen in previous work.²⁹ For the viscosity, the experimental correlation is only valid in a small temperature range. In this range, the RIM model performs the best, deviating less than 5 %

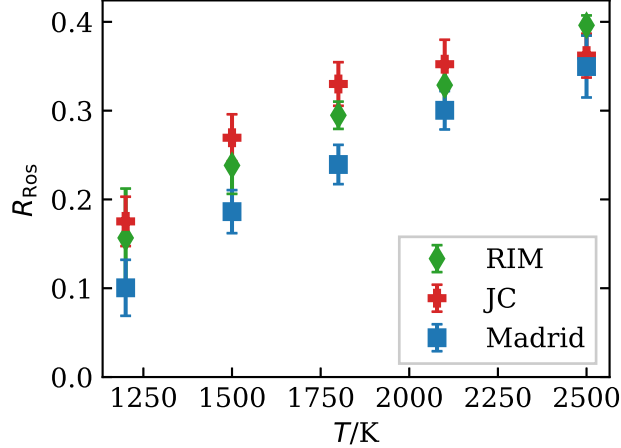


FIG. 3. Correlation coefficient of potential energy and virial for three NaCl models at the density of the 0.1 MPa, 1200 K simulation: $24.00 \text{ mol}\cdot\text{dm}^{-3}$ for the RIM model, $22.96 \text{ mol}\cdot\text{dm}^{-3}$ for the JC model, and $21.58 \text{ mol}\cdot\text{dm}^{-3}$ for the Madrid model.

from experiments, while the JC model overpredicts the viscosity by 70 % and the Madrid model underpredicts it by 15 %. As mentioned earlier, it is not surprising that the Madrid model has the lowest viscosity due to the scaled charges. The RIM model performs the best for both residual entropy and viscosity. Unlike the JC and Madrid models, the RIM model was fit solely to pure salt data, although only using solid phase properties. From Figure 2, it can be seen that an extrapolation of the viscosity correlation crosses through the data at higher temperatures. This extrapolation behavior is likely incorrect and indicates that a stronger theoretical basis for viscosity correlations is needed.

To test the applicability of entropy scaling, values of R_{Ros} for the NaCl models were calculated. As can be seen from Figure 3, R_{Ros} is closer to zero than to one, with a maximum around 0.4. As the temperature increases, R_{Ros} increases and should approach 1 at infinite temperature. This is because repulsive interactions dominate at higher temperatures, and an inverse power-law repulsion will follow entropy scaling perfectly. A model with exponential repulsion, such as the RIM, will still approximately follow entropy scaling, with R_{Ros} higher than 0.8 over much of the phase diagram.³⁷ A similar plot of R_{Ros} versus temperature at constant pressure does not show an increase in R_{Ros} with temperature. The reason is that the increase in volume with temperature decreases the repulsive interactions in the system.

At the temperatures of interest for this work, the low values of R_{Ros} in Figure 3 indicate

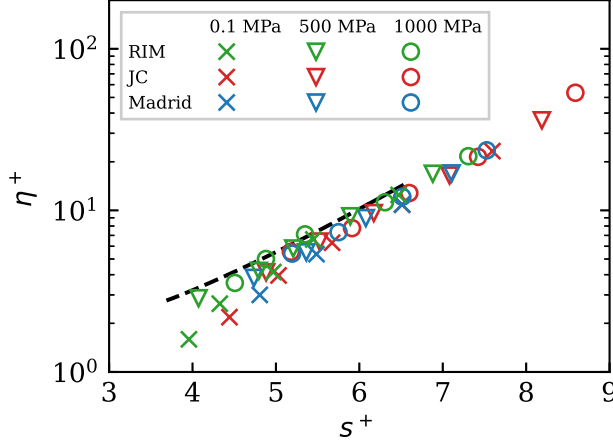


FIG. 4. Entropy scaling behavior of all three NaCl models. The solid curve represents the scaling calculated from the experimental correlations,^{33,36} and the dashed curve represents the extrapolation of the experiments.

that molten salts do not follow isomorph theory, and entropy scaling is not expected to apply. However, when the reduced viscosity is plotted against the residual entropy, all of the data from 0.1 MPa to 1000 MPa and 1200 K to 2500 K collapse onto one curve. This entropy scaling behavior for the NaCl models is shown in Figure 4. The data cover a viscosity range of two orders of magnitude, from 0.014 to 3.3 mPa·s. The experimental scaling curves are from the NIST-JANAF tables³³ and published viscosity correlations.³⁶ As can be seen, the data begin to spread out at smaller values of s^+ . This corresponds to the simulations at higher temperature and lower densities and is a sign that entropy scaling is beginning to break down.

To further investigate this behavior, simulations were run at different densities along a 4000 K isotherm. From previous calculations of phase equilibrium, this temperature should be well above the critical point which is expected to be lower than 3500 K for all of the models.²⁹ As seen in Figure 5, the residual entropy initially approaches zero as the density decreases, which is expected since the system becomes more similar to the non-interacting ideal gas state at low density. However, as the density further decreases, the residual entropy begins to move away from zero. This is coupled with peaks in the heat capacity and indicates that ion chains and pairs are forming, as seen in the simulation snapshot in Figure 6. When plotted on the entropy scaling figure, as in Figure 7, the loop in the residual entropy does not

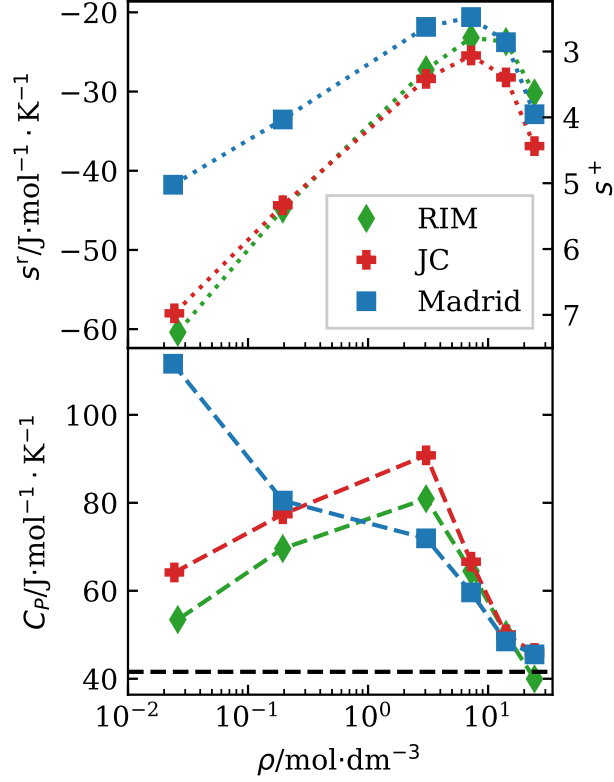


FIG. 5. Residual entropy and heat capacity of the three NaCl models along a 4000 K isotherm. The black dashed line indicates the ideal gas C_P , and the colored lines connecting the points are included to guide the eye.

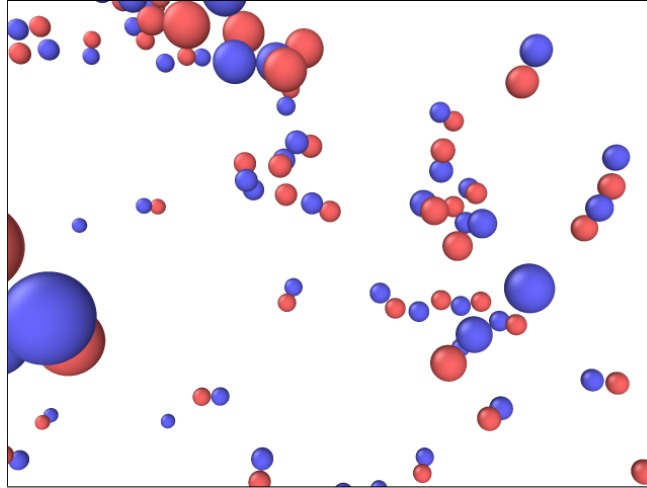


FIG. 6. Snapshot of the JC model at 4000 K and a density of $0.195 \text{ mol}\cdot\text{dm}^{-3}$. The red particles are Na^+ ions and the blue particles are Cl^- ions. The sizes of the particles correspond to their closeness to the front of the three-dimensional cell. The visualization is produced using OVITO.³⁸

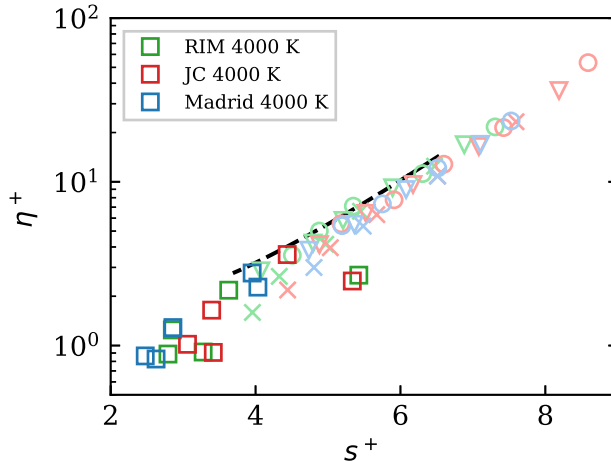


FIG. 7. Entropy scaling behavior of all three NaCl models along a 4000 K isotherm. The light-colored symbols are the same as in Figure 4. The solid curve represents the experimental scaling,^{33,36} and the dashed curve represents the extrapolation of the experiments.

fall back on the same curve as before for the JC and RIM models, indicating that entropy scaling no longer applies. Entropy scaling has been shown to break down for network-forming fluids,³⁹ and further support for that is shown by entropy scaling failing more for the full-charge models which have stronger ion pairing. However, the fact that the reduced viscosity also increases when s^+ does indicates that there is still a link between these properties.

The entropy scaling behavior is very similar for the three NaCl models shown in Figure 4. The RIM model is systematically above the JC and Madrid models, but by an amount similar to the uncertainty. These three models cover a range of functional forms and fitting targets and all fall slightly below the experimental scaling curve. This indicates that some additional physics, such as polarization, is likely necessary to create a molecular model that is able to better match experiments.

The entropy scaling behavior of the RIM model for a number of monovalent salts is shown in Figure 8. The experimental scaling curves are again from the NIST-JANAF tables³³ and published viscosity correlations.³⁶ All of the salts behave similarly to NaCl. However, there is more scatter between the salts than within each salt. This indicates that all the simple monovalent salts we have studied approximately exhibit entropy scaling, but the scaling relationships differ somewhat among the salts. Comparing the experimental curves at 0.1 MPa to the simulation results at 0.1 MPa shows that the simulations have

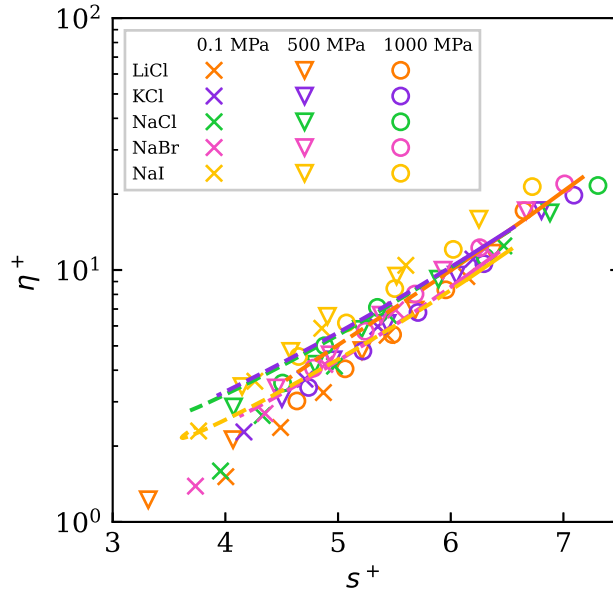


FIG. 8. Entropy scaling behavior of RIM models for different monovalent salts. The solid curves represent the experimental scalings,^{33,36} and the dashed curves represent the extrapolations of the experiments.

slightly more scatter between salts than the experiments. However, Figure 8 suggests that it could be possible to use the residual entropy to predict the viscosity behavior of an unstudied monovalent salt within about 10 %. The residual entropy of a molten salt can be experimentally calculated from an equation of state or estimated from the structure factor.⁴⁰

V. CONCLUSIONS

The good performance of entropy scaling for molten salt systems is unexpected based on current entropy scaling theories. This indicates that a strong correlation between the potential energy and virial is a sufficient but not necessary condition for entropy scaling to apply. Further theoretical investigation is needed to better understand the applicability of entropy scaling.

All of the investigated NaCl models were found to have similar entropy scaling, despite the differences in the models. However, this scaling behavior was not the same as the experimental entropy scaling, indicating that some physics is missing for molecular models to better capture experimental dynamic and thermodynamic properties.

Even without understanding the theoretical basis, the fact that entropy scaling works for molten salts means that it is possible to develop viscosity correlations valid over much larger temperature and pressure ranges. These viscosity correlations will need to be coupled with accurate molten salt equations of state for obtaining the residual entropy. Entropy scaling breaks down for molten salts as the density becomes low. This breakdown of entropy scaling is due to the formation of ion pairs and chains, meaning that the fluid is no longer homogeneous. These conditions are extreme and unlikely to be found in real applications, but this phenomenon places a limit on the validity of any correlation for viscosity. Future studies are needed to determine if entropy scaling can be used to correlate other dynamic properties of molten salts such as diffusivity and ionic conductivity.

VI. SUPPLEMENTARY MATERIAL

The Supplementary Material includes the model parameters, tables of simulation results, and example simulation input scripts.

VII. AUTHOR DECLARATIONS

A. Conflict of interest

The authors have no conflicts to disclose.

VIII. DATA AVAILABILITY

The data that supports the findings of this study are available in the Supplementary Material.

REFERENCES

- ¹A. L. Dicks, “Molten carbonate fuel cells,” *Curr. Opin. Solid State Mater. Sci.* **8**, 379–383 (2004).
- ²P. Masset and R. A. Guidotti, “Thermal activated (thermal) battery technology Part II. Molten salt electrolytes,” *J. Power Sources* **164**, 397–414 (2007).

- ³J. Serp, M. Allibert, O. Beneš, S. Delpech, O. Feynberg, V. Ghetta, D. Heuer, D. Holcomb, V. Ignatiev, J. L. Kloosterman, L. Luzzi, E. Merle-Lucotte, J. Uhlíř, R. Yoshioka, and D. Zhimin, “The molten salt reactor (MSR) in generation IV: Overview and perspectives,” *Prog. Nucl. Energy* **77**, 308–319 (2014).
- ⁴U. Herrmann, B. Kelly, and H. Price, “Two-tank molten salt storage for parabolic trough solar power plants,” *Energy* **29**, 883–893 (2004).
- ⁵J. C. Dyre, “Perspective: Excess-entropy scaling,” *J. Chem. Phys.* **149**, 210901 (2018).
- ⁶I. H. Bell, “Entropy Scaling of Viscosity - I: A Case Study of Propane,” *J. Chem. Eng. Data* **65**, 3203–3215 (2020).
- ⁷N. P. Bailey, U. R. Pedersen, N. Gnan, T. B. Schrøder, and J. C. Dyre, “Pressure-energy correlations in liquids. I. Results from computer simulations,” *J. Chem. Phys.* **129**, 184507 (2008).
- ⁸T. B. Schrøder and J. C. Dyre, “Simplicity of condensed matter at its core: Generic definition of a Roskilde-simple system,” *J. Chem. Phys.* **141**, 204502 (2014).
- ⁹N. Gnan, T. B. Schrøder, U. R. Pedersen, N. P. Bailey, and J. C. Dyre, “Pressure-energy correlations in liquids. IV. “Isomorphs” in liquid phase diagrams,” *J. Chem. Phys.* **131**, 234504 (2009).
- ¹⁰I. H. Bell, R. Messerly, M. Thol, L. Costigliola, and J. C. Dyre, “Modified Entropy Scaling of the Transport Properties of the Lennard-Jones Fluid,” *J. Phys. Chem. B* **123**, 6345–6363 (2019).
- ¹¹R. Sharma, S. N. Chakraborty, and C. Chakravarty, “Entropy, diffusivity, and structural order in liquids with waterlike anomalies,” *J. Chem. Phys.* **125**, 204501 (2006).
- ¹²M. Agarwal and C. Chakravarty, “Relationship between structure, entropy, and mobility in network-forming ionic melts,” *Phys. Rev. E* **79**, 030202 (2009).
- ¹³M. Agarwal, A. Ganguly, and C. Chakravarty, “Transport properties of tetrahedral, network-forming ionic melts,” *J. Phys. Chem. B* **113**, 15284–15292 (2009).
- ¹⁴B. S. Jabes and C. Chakravarty, “Relating composition, structural order, entropy and transport in multi-component molten salts,” *J. Chem. Phys.* **136**, 144507 (2012).
- ¹⁵P. A. Knudsen, K. Niss, and N. P. Bailey, “Quantifying dynamical and structural invariance in a simple molten salt model,” *J. Chem. Phys.* **155**, 054506 (2021).
- ¹⁶H. Wang, R. S. DeFever, Y. Zhang, S. Roy, V. Bryantsev, C. S. Margulis, and E. J. Maginn, “Comparison of Fixed Charge and Polarizable Models for Predicting the Structural,

- Thermodynamic and Transport Properties of Molten Alkali Chlorides,” *J. Chem. Phys.* **153**, 214502 (2020).
- ¹⁷R. E. Young and J. P. O’Connell, “An Empirical Corresponding States Correlation of Densities and Transport Properties of 1-1 Alkali Metal Molten Salts,” *Ind. Eng. Chem. Fund.* **10**, 418–423 (1971).
- ¹⁸J. E. Mayer, “Dispersion and Polarizability and the van der Waals Potential in the Alkali Halides,” *J. Chem. Phys.* **1**, 270–279 (1933).
- ¹⁹M. P. Tosi and F. G. Fumi, “Ionic Sizes and Born Repulsive Parameters in the NaCl-Type Alkali Halides - II: The Generalized Huggins-Mayer Form,” *J. Phys. Chem. Solids* **25**, 45–52 (1964).
- ²⁰I. S. Joung and T. E. Cheatham, “Determination of alkali and halide monovalent ion parameters for use in explicitly solvated biomolecular simulations,” *J. Phys. Chem. B* **112**, 9020–9041 (2008).
- ²¹A. L. Benavides, M. A. Portillo, V. C. Chamorro, J. R. Espinosa, J. L. F. Abascal, and C. Vega, “A potential model for sodium chloride solutions based on the TIP4P/2005 water model,” *J. Chem. Phys.* **147**, 104501 (2017).
- ²²Z. Mester and A. Z. Panagiotopoulos, “Mean ionic activity coefficients in aqueous NaCl solutions from molecular dynamics simulations,” *J. Chem. Phys.* **142**, 044507 (2015).
- ²³J. Pátek, J. Hrubý, J. Klomfar, M. Součková, and A. H. Harvey, “Reference Correlations for Thermophysical Properties of Liquid Water at 0.1 MPa,” *J. Phys. Chem. Ref. Data* **38**, 21–29 (2009).
- ²⁴I. Leontyev and A. Stuchebrukhov, “Accounting for electronic polarization in non-polarizable force fields,” *Phys. Chem. Chem. Phys.* **13**, 2613 (2011).
- ²⁵A. H. Harvey, J. S. Gallagher, and J. M. H. Levelt Sengers, “Revised Formulation for the Refractive Index of Water and Steam as a Function of Wavelength, Temperature and Density,” *J. Phys. Chem. Ref. Data* **27**, 761–774 (1998).
- ²⁶M.-T. Nguyen, V.-A. Glezakou, J. Lonergan, B. McNamara, P. D. Paviet, and R. Rousseau, “Ab initio molecular dynamics assessment of thermodynamic and transport properties in (K,Li)Cl and (K, Na)Cl molten salt mixtures,” *J. Mol. Liq.* **326**, 115262 (2021).
- ²⁷S. Yue and A. Z. Panagiotopoulos, “Dynamic properties of aqueous electrolyte solutions from non-polarisable, polarisable, and scaled-charge models,” *Mol. Phys.* **117**, 3538–3549

- (2019).
- ²⁸T. G. A. Youngs and C. Hardacre, “Application of Static Charge Transfer within an Ionic-Liquid Force Field and Its Effect on Structure and Dynamics,” *ChemPhysChem* **9**, 1548–1558 (2008).
 - ²⁹D. Kussainova, A. Mondal, J. M. Young, S. Yue, and A. Z. Panagiotopoulos, “Molecular simulation of liquid-vapor coexistence for NaCl: Full-charge vs scaled-charge interaction models,” *J. Chem. Phys.* **153**, 024501 (2020).
 - ³⁰A. P. Thompson, H. M. Aktulga, R. Berger, D. S. Bolintineanu, W. M. Brown, P. S. Crozier, P. J. in ’t Veld, A. Kohlmeyer, S. G. Moore, T. D. Nguyen, R. Shan, M. J. Stevens, J. Tranchida, C. Trott, and S. J. Plimpton, “LAMMPS - a flexible simulation tool for particle-based materials modeling at the atomic, meso, and continuum scales,” *Comput. Phys. Commun.* **271**, 108171 (2022).
 - ³¹E. J. Maginn, R. A. Messerly, D. J. Carlson, D. R. Roe, and J. R. Elliott, “Best Practices for Computing Transport Properties 1. Self-Diffusivity and Viscosity from Equilibrium Molecular Dynamics [Article v1.0],” *Living J. Comp. Mol. Sci.* **1**, 6324 (2019).
 - ³²M. R. Shirts and J. D. Chodera, “Statistically optimal analysis of samples from multiple equilibrium states,” *J. Chem. Phys.* **129**, 124105 (2008), arXiv:0801.1426.
 - ³³M. W. Chase, Jr., *NIST-JANAF Thermochemical Tables*, 4th ed. (American Institute of Physics, Woodbury, NY, 1998).
 - ³⁴G. J. Janz, “Thermodynamic and transport properties for molten salts: Correlation equations for critically evaluated density, surface tension, electrical conductance, and viscosity data,” *J. Phys. Chem. Ref. Data* **17**, Suppl. 2 (1988).
 - ³⁵P. Ströker, R. Hellmann, and K. Meier, “Systematic formulation of thermodynamic properties in the NpT ensemble,” *Phys. Rev. E* **103**, 023305 (2021).
 - ³⁶K. A. Tasidou, C. D. Chliatzou, M. J. Assael, K. D. Antoniadis, S. K. Mylona, M. L. Huber, and W. A. Wakeham, “Reference Correlations for the Viscosity of 13 Inorganic Molten Salts,” *J. Phys. Chem. Ref. Data* **48**, 013101 (2019).
 - ³⁷J. C. Dyre, “Simple liquids’ quasiuniversality and the hard-sphere paradigm,” *J. Phys. Condens. Matter* **28**, 323001 (2016).
 - ³⁸A. Stukowski, “Visualization and analysis of atomistic simulation data with OVITO—the Open Visualization Tool,” *Modell. Simul. Mater. Sci. Eng.* **18**, 015012 (2010).

- ³⁹R. Chopra, T. M. Truskett, and J. R. Errington, “On the Use of Excess Entropy Scaling to Describe the Dynamic Properties of Water,” *J. Phys. Chem. B* **114**, 10558–10566 (2010).
- ⁴⁰B. B. Laird and A. D. J. Haymet, “Calculation of the entropy from multiparticle correlation functions,” *Phys. Rev. A* **45**, 5680–5689 (1992).