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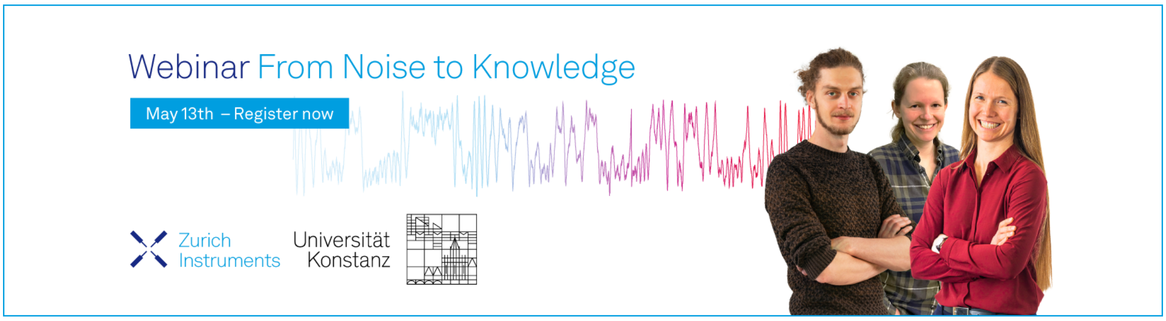

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ABSTRACT

The shift in the temperature of maximum in density (TMD) at room pressure of aqueous solutions of a set of five salts containing NO_3^- and/or NH_4^+ groups is studied both through experiments and through molecular dynamics simulations using the Madrid-2019 force field for ions and the TIP4P/2005 model for water. The experiments demonstrate the potential transferability and limitations of the Madrid-2019 force field for nitrate and ammonium ions recently developed by our group at different temperatures and add updated information to the reported datasets of TMDs for strong electrolytes. By using the Despretz law, individual ion contributions are extracted for predictive purposes from the experimental values of the shift in the TMD. Interesting findings for the behavior of the shift in the TMD in nitrate salts expose that this property might be particularly challenging for modelization approaches when dealing with polyatomic species.

The presence of strong electrolytes in aqueous solutions influences both the structure and thermodynamic properties of pristine bulk water.[1–8] A particularly interesting property is the lowering of the temperature of maximum in density of water ($\Delta = \text{TMD}_{solution} - \text{TMD}_{water}$), plausibly originated by the modification of the *locus* of the high-to-low density liquid–liquid transition.[9–17] Consequently, the experimental exploration of supercooled electrolytic solutions might be a route to investigate this baffling transition[18] and to obtain indirect information about the specific tetrahedricity changes provoked by the addition of ions to water.[19] Such a rearrangement strongly depends on the chemical features of the ions at play and on their concentration. For low concentrated solutions, such dependencies are enclosed by the simple Despretz law[20,21] stating that a linear relation of the following form is fulfilled:

$$\Delta = K_m m, \tag{1}$$

being m the molality of the solution (i.e., the number of moles of solute per kilogram of solvent) and K_m the Despretz constant in molality units. In this diluted regime, it is plausible to assume that the solvent effectively screen ion–ion interactions, and an "additive group contribution" approach has been frequently used in the literature, i.e., K_m is split into individual ion contributions ($K_m^{\pm}$) as[22]

$$K_m = \nu_+ K_m^+ + \nu_- K_m^-, \tag{2}$$

being ν_+ and ν_- the stoichiometric coefficients of the cation and the anion, respectively. Obviously, while K_m is unique for a given salt, the specific values of $K_m^{\pm}$ are not unequivocally defined, being a reference value required. In our recent works,[22,23] the reference ion was selected to be the Li^+ cation, for which we assigned $K_m^+ = -3$ K kg/mol.

By combining experimental and simulation results, our group has successfully established and discussed in the framework of the Despretz approximation the $K_m^{\pm}$ values for several ions, namely alkali and alkaline-earth metal cations and halide and sulfate anions. These results served to validate the Madrid-2019 force field against the prediction of the TMD for a wide ensemble of salts.[22,23] This force field uses a scaled charge of $\pm 0.85e$ per unit of formal charge to account for the solvent screening in the spirit of Leontyev and Stuchebrukhov approach[24–26] in combination with the TIP4P/2005 water model[27] and is able to quantitatively reproduce the TMD of pure water, among many other properties.[22,28–30] However, most ions studied to date by us are atomic or bear a spherical or *quasi*-spherical T_d shape (i.e., SO_4^{2-}). This feature leads to well defined spherically symmetric hydration shells, and differences between experiments and simulations are discussed in terms of the lack of polarizability of some big ions. Provided that we have recently developed an extension of the Madrid-2019 force field for NO_3^- and NH_4^+ that successfully reproduces the densities as a function of the concentration, the ion–ion and ion–water structure, or the transport coefficients,[31] we have extended this fruitful approach to determine from experiments and evaluate from molecular dynamics simulations the TMD of five soluble and widely used salts comprised by polyatomic nitrogenated ions (NO_3^- and/or NH_4^+) and a counterion, namely $NaNO_3$, KNO_3, NH_4NO_3, NH_4Cl, and $(NH_4)_2SO_4$. Both simulation and experimental details as long as the raw datasets in tabular form are provided in the supplementary material.

A summary of the computational and experimental TMD values and the densities at the TMD is given in Table I for all the salts and concentrations considered here. In Fig. 1(a), the results for 1 *m* solutions are presented. As observed, simulations are able to describe fairly well the temperature dependence of the density of the solutions down to the density maximum. In particular, deviations between the experimental and calculated densities at their maxima are always smaller than 0.4%, a figure similar to that found for the Madrid-2019 model in recent papers.[23,32] This moderate offset between the experimental and simulated densities in the covered temperature range is indicative of the transferability of the intermolecular potential in the supercooled regime, at least to determine densities. Furthermore, the predictions of the TMD values for the ammonium salts are remarkable. Hence, the values of Δ have been split into individual contributions employing the previously published values of $K_m^{\pm}$ for Cl^- and SO_4^{2-}.[23] In brief, the experimental value of Δ would serve to evaluate K_m from the Despretz law for each salt. Applying Eq. (1) and the reported $K_m^{\pm}$ values,[22] the contributions of ammonium to Δ might be straightforwardly calculated by comparing the TMD shifts for NH_4Cl and $(NH_4)_2SO_4$. We found that, on average, $\langle K_m^+ \rangle = -3.7$ K kg/mol, which is a (small) value more typical of an anion in our group contribution scale.[23]

However, for nitrate salts, simulations progressively overestimated the experimental densities as the temperature decreases and the TMD is infraestimated by more than ~5 K at 1 *m*. In other

TABLE I. Experimental and simulated values of the temperature of maximum in density and the density at the TMD (ρ_{max}) of the electrolyte solutions. Dev. and Dev. (%) stand for deviations of the experimental from simulated results and the deviation percentage [i.e., $100 \times (TMD_{exp} - TMD_{MD})/TMD_{exp}$ for the TMD, in Kelvin], respectively. The values in bold indicate that the model is not quite successful in reproducing the experimental values of the TMD, since the difference between the experimental and simulated TMD values differ by more than 3 K (i.e., higher than the combined experimental and simulations uncertainties). Performing simulations of systems for which the expected $\Delta \lesssim 3$ K was avoided.

		TMD (K)				ρ_{max} (kg/m^3)			
Salt	Molality (mol/kg)	Exp.	Madrid-2019	Dev.	Dev. (%)	Exp.	Madrid-2019	Dev.	Dev. (%)
NH_4Cl	1.000	269.7	271.1	−1.4	−0.5	1017.1	1017.1	<0.1	<0.1
	0.500	273.3	274.2	−0.9	−0.3	1008.9	1009.2	−0.3	<−0.1
	0.237	275.3	⋯	⋯	⋯	1004.3	⋯	⋯	⋯
	0.140	276.1	⋯	⋯	⋯	1002.6	⋯	⋯	⋯
$(NH_4)_2SO_4$	1.000	255.1	257.2	−2.1	−0.8	1073.0	1074.2	−1.2	−0.1
	0.500	266.7	266.0	0.7	0.3	1038.7	1040.0	−1.3	−0.1
	0.134	274.2	⋯	⋯	⋯	1010.9	⋯	⋯	⋯
	0.070	275.6	⋯	⋯	⋯	1005.8	⋯	⋯	⋯
	0.040	276.3	⋯	⋯	⋯	1003.4	⋯	⋯	⋯
NH_4NO_3	1.000	263.4	261.2	2.2	0.8	1033.5	1034.8	−1.3	−0.1
	0.150	275.1	274.3	0.8	0.3	1005.2	1005.9	−0.7	<−0.1
$NaNO_3$	1.000	256.9	250.6	**6.3**	2.5	1059.3	1062.6	−3.3	−0.3
	0.700	263.8	259.1	**4.7**	1.8	1041.9	1043.9	−2.0	−0.2
	0.500	267.4	263.2	**4.2**	1.6	1030.0	1031.5	−1.5	−0.1
	0.150	274.1	273.6	0.5	0.2	1009.1	1009.9	−0.8	<−0.1
	0.090	275.4	⋯	⋯	⋯	1005.5	⋯	⋯	⋯
	0.054	276.1	⋯	⋯	⋯	1003.3	⋯	⋯	⋯
	0.032	276.5	⋯	⋯	⋯	1001.9	⋯	⋯	⋯
	0.014	276.9	⋯	⋯	⋯	1000.8	⋯	⋯	⋯
KNO_3	1.000	261.1	255.6	**5.5**	2.1	1062.8	1066.0	−3.2	−0.3
	0.150	274.4	273.5	0.9	0.3	1009.9	1010.7	−0.8	<−0.1

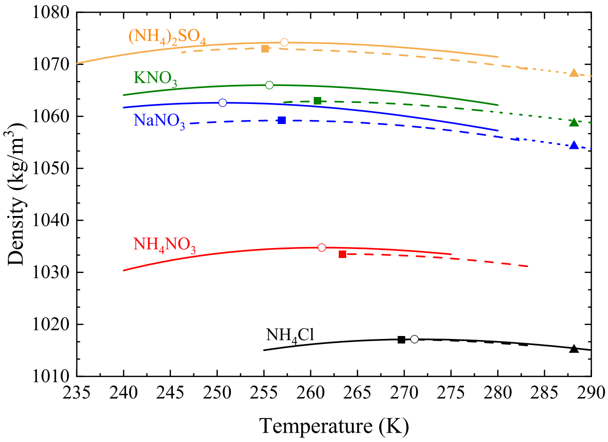

FIG. 1. Density for the salt solutions considered in this work at 1 *m* as a function of temperature at room pressure. Solid lines: third-order polynomial fit to the molecular dynamics data obtained with the Madrid-2019 model.[31–34] Dashed lines: raw experimental data obtained in this work. TMDs are represented by filled squares (experiment) and empty circles (simulations). The full up-pointing triangles stand for experimental data at 288.15 K from Ref. 35, and the dotted lines are the corresponding extrapolation from the fit to the experimental data.

words, the corresponding K_m constants for nitrate salts largely differ from that obtained from simulations, with the notable exception of NH_4NO_3. For this electrolyte, the small overestimation of the computed TMD for salts containing NH_4^+ is partly compensating the severe underestimation observed for nitrates. Such an intriguing result pinpointed two possible scenarios: (i) limitations of the non-polarizable rigid force field (i.e., lack of polarizability, incorrect description of high order multipolar moments, excluded volume, and many body effects) that become more evident at low temperatures; (ii) the Despretz law stops being fulfilled at 1 *m* for these electrolytes. To solve this issue, we performed further experiments and simulations for more diluted solutions (see Table I and the supplementary material). Before proceeding for nitrates, we performed experiments for NH_4Cl, $(NH_4)_2SO_4$, and the important case of NaCl to confirm that, indeed, the Despretz law is fulfilled for these salts up to 1 *m*. The results for the variation of Δ with *m*, shown in Fig. S1, happily confirmed this thought, at least in these cases. It should be pointed out that, for NaCl, our experimental results differ from those reported in Ref. 36 by about 5 K kg/mol (i.e., the Despretz constant obtained from our experiments for NaCl is −14.4 K kg/mol, while a value of −9.2 K kg/mol is reported in Ref. 36). For this important salt, the new experimental (m, Δ) points are (0.2,−2.83), (0.14,−1.92), (0.09,−1.26), and (0.05,−0.61); see Fig. S1.

Then, we carried out experiments for the three nitrate salts at 0.15 *m*. In Fig. S2 and Table I, the nice agreement between experiments and simulations is shown. Although it is tentative to ascribe this effect to the diminution of the interionic interactions in the diluted regime, it must be emphasized that even when the relative deviation of Δ (in absolute values) obtained from simulation diminishes with *m*, the values of $K_m = \Delta/m$ still differ by ∼25%. That is, the hypothesis (i) is behind the discrepancies initially found at 1 *m*. To reconfirm this point, we performed supplementary experiments and simulations in a range of concentrations for $NaNO_3$, i.e., 1, 0.70, 0.50, 0.15, 0.12, 0.09, 0.054, and 0.014 *m*. In Fig. 2(a), we plot the density–temperature profile for some of these concentrations for $NaNO_3$. As shown in Fig. 2(b), Δ diminishes with *m* in a linear way ($R^2 = 0.999$), with a slope of $K_m = -19.7$ K kg/mol consistent with Ref. 36 and with a large difference with that obtained from simulations. The linear trend of the experimental data allows us to extract an average $\langle K_m^- \rangle = -8.1$ K kg/mol for the nitrate anion that was used to extract the group contribution predictions for Δ. A comparison between the values of Δ determined experimentally (Δ_{exptl}) and those obtained from molecular dynamics (Δ_{MD}) and from the group contribution approach (Δ_{group}^{Exp}) is shown in Table II. Although it is possible to reproduce the experimental shift in the TMD with a deviation from the experimental value of at most 2 K for all the cases from the group contribution approach, the values obtained from simulations show remarkable deviations. Further work is needed

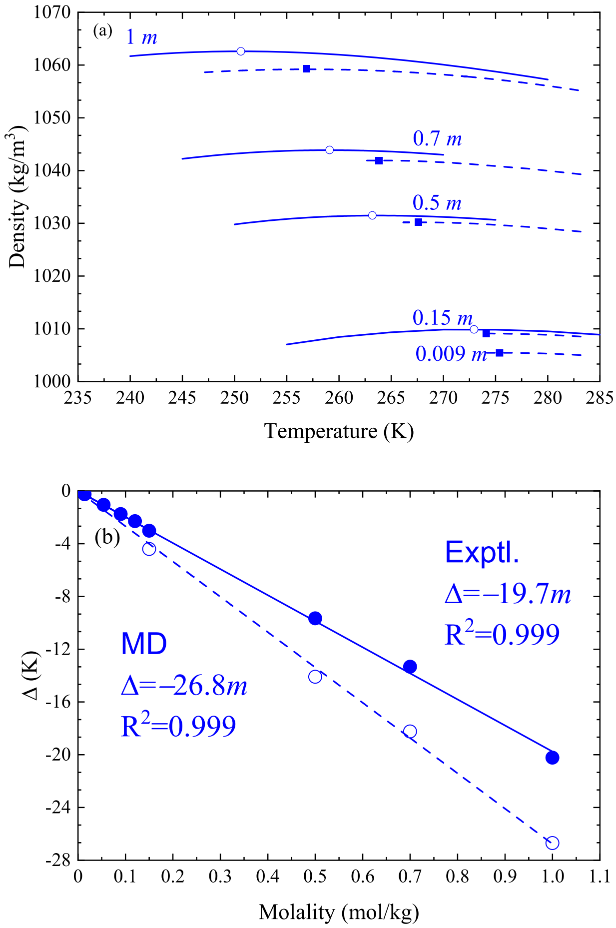

FIG. 2. (a) Density for the $NaNO_3$ solutions considered in this work as a function of temperature at room pressure. Solid lines: third-order polynomial fit to the molecular dynamics data obtained with the Madrid-2019 model in Refs. 31–34. Dashed lines: raw experimental data obtained in this work. TMDs are represented by filled squares (experiments) and empty circles (simulations). (b) Variation of Δ with *m* for sodium nitrate solutions. The continuous line and full symbols stand for a linear fit weighted by the experimental uncertainties, while the empty symbols and dashed line have the equivalent meaning for the molecular dynamics results.

TABLE II. Shift in the TMD (in K) of the salt solutions measured experimentally, evaluated from molecular dynamics simulations, and calculated from the individual group contribution approach, the latter being obtained from the experimental values of $\langle K_m^+ \rangle$ = −3.7 K kg/mol and $\langle K_m^- \rangle$ = −8.1 K kg/mol for the ammonium and nitrate ions, respectively. The $K_m^\pm$ values for the counterions were taken as −3.2, −15.8, −11.6, and −8.8 K kg/mol for Cl^-, SO_4^{2-}, Na^+, and K^+, respectively, as reported in Ref. 23. The value of TMD_{water}^{MD} is set to 277.3 K according to Ref. 22. The value of TMD_{water}^{exp} was set to 277.13 K.

Salt	Molality	Δ_{Exptl}	Δ_{MD}	Δ_{group}^{Exp}
NH_4Cl	1.000	−7.4	−6.2	−6.9
	0.500	−3.8	−3.1	−3.5
	0.237	−1.8	⋯	−1.7
	0.140	−1.0	⋯	−1.0
$(NH_4)_2SO_4$	1.000	−22.0	−20.1	−23.2
	0.500	−10.4	−11.3	−11.6
	0.134	−2.9	⋯	−3.0
	0.070	−1.5	⋯	−1.6
	0.040	−0.8	⋯	−0.9
NH_4NO_3	1.000	−13.7	−16.1	−11.8
	0.150	−2.0	−3.0	−1.8
$NaNO_3$	1.000	−20.2	−26.7	−19.7
	0.700	−13.3	−18.2	−13.8
	0.500	−9.7	−14.5	−9.9
	0.150	−3.0	−4.4	−3.0
	0.090	−1.7	⋯	−1.8
	0.054	−1.0	⋯	−1.1
	0.032	−0.6	⋯	−0.6
	0.014	−0.2	⋯	−0.3
KNO_3	1.000	−16.0	−21.7	−16.9
	0.150	−2.7	−3.8	−2.5

to understand the origin of the failure of the force field predictions for NO_3^-. This anion is somewhat different to other species: it presents a planar geometry (in contrast to monoatomic ions and the *quasi*-spherical sulfate and ammonium ions), the presence of three potentially hydratable oxygen atoms facilitates to hold ~20–25 water molecules per ion in its close surroundings (see Ref. 31 and references therein), and it may have a high number of anion–anion and anion–cation pairs. The failure of the force field brings another consequence: the TMD of nitrate salts is quite sensitive to the details of the force field and can be used as a target property in the future.

In brief, we provide updated, accurate, and useful experimental data of TMDs and of the dependence of the density on temperature for a selected set of five soluble nitrate and ammonium salts dissolved in water. The results of this work clearly show that the Despretz law [see Eq. (1)] holds for all the salts considered in this work for concentrations up to 1 m. The results can be considered a benchmark for the development of other force fields for these polyatomic ions in relation to the desirable ability to predict the TMD of electrolyte solutions. The capacity of the Madrid-2019 force field for predicting TMDs is directly tested against these experiments. We demonstrate that this model predicts extraordinarily well the densities for a wide range of temperatures and both the TMD and the density at the maximum for ammonium salts even at 1 m, with deviations from the experimental data of less than 0.1% for the density at the TMD and 1% for the TMD, respectively. While the model is very accurate when dealing with ammonium salts, it is interesting to note that it is not in predicting the TMD of nitrate salts. A comparison between experiments and simulations shows different Despretz constants for this ion that presumably arises from the interplay between the complex scenario that entails the hydration of the NO_3^- ion and its interionic interactions that are a consequence of the multiple contact sites within the molecule. By collecting all the experimental values, we were able to establish the contribution of both ions to the TMD following a group contribution approach. These findings indicate that research in the development of force fields for ions should pay special attention to predict the TMD when dealing with polyatomic species.

In the supplementary material, we have collected the experimental results for the densities of all salts considered in this work. Details about the experiments and molecular dynamics simulations are also provided.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

S. Blazquez: Formal analysis (equal); Investigation (equal); Methodology (equal); Writing – review & editing (equal). **M. de Lucas**: Formal analysis (equal); Investigation (equal); Methodology (equal). **C. Vega**: Conceptualization (equal); Funding acquisition (equal); Writing – review & editing (equal). **J. Troncoso**: Data curation (equal); Funding acquisition (equal); Investigation (equal); Methodology (equal); Writing – review & editing (equal). **F. Gámez**: Conceptualization (equal); Funding acquisition (equal); Investigation (equal); Methodology (equal); Supervision (equal); Writing – original draft (equal); Writing – review & editing (equal).

DATA AVAILABILITY

The data that supports the findings of this study are available within the article and its supplementary material.

REFERENCES

[1] P. Gallo, M. Rovere, and D. Corradini, Phys. Chem. Chem. Phys. **13**, 19814 (2011).

[2] C. Zhang, S. Yue, A. Z. Panagiotopoulos, M. L. Klein, and X. Wu, Nat. Commun. **13**, 822 (2022).

[3] R. Mancinelli, A. Botti, F. Bruni, M. A. Ricci, and A. K. Soper, Phys. Chem. Chem. Phys. **9**, 2959 (2007).

[4] J. Holzmann, R. Ludwig, A. Geiger, and D. Paschek, Angew. Chem., Int. Ed. **46**, 8907 (2007).

[5] M. T. H. Nguyen, O. Tichacek, H. Martinez-Seara, P. E. Mason, and P. Jungwirth, J. Phys. Chem. B **125**, 3153 (2021).

[6] R. Mancinelli, A. Botti, F. Bruni, M. A. Ricci, and A. K. Soper, J. Phys. Chem. B **111**, 13570 (2007).

[7] I. Pethes, J. Mol. Liq. **361**, 119660 (2022).

[8] S. Wang, J. Jacquemin, P. Husson, C. Hardacre, and M. F. Costa Gomes, J. Chem. Thermodyn. **41**, 1206 (2009).

[9] P. H. Poole, F. Sciortino, U. Essmann, and H. E. Stanley, Nature **360**, 324 (1992).

[10] G. Pallares, M. E. M. Azouzi, M. A. González, J. L. Aragonés, J. L. F. Abascal, C. Valeriani, and F. Caupin, Proc. Natl. Acad. Sci. U. S. A. **111**, 7936 (2014).

[11] T. E. Gartner, L. Zhang, P. M. Piaggi, R. Car, A. Z. Panagiotopoulos, and P. G. Debenedetti, Proc. Natl. Acad. Sci. U. S. A. **117**, 26040 (2020).

[12] L. Xu, P. Kumar, S. V. Buldyrev, S. H. Chen, P. H. Poole, F. Sciortino, and H. E. Stanley, Proc. Natl. Acad. Sci. U. S. A. **102**, 16558 (2005).

[13] A. Nilsson and L. G. M. Pettersson, Nat. Commun. **6**, 8998 (2015).

[14] R. J. Speedy and C. A. Angell, J. Chem. Phys. **65**, 851 (1976).

[15] H. Tanaka, Eur. Phys. J. E: Soft Matter Biol. Phys. **35**, 113 (2012).

[16] P. Gallo, K. Amann-Winkel, C. A. Angell, M. A. Anisimov, F. Caupin, C. Chakravarty, E. Lascaris, T. Loerting, A. Z. Panagiotopoulos, J. Russo *et al.*, Chem. Rev. **116**, 7463 (2016).

[17] J. Russo, K. Akahane, and H. Tanaka, Proc. Natl. Acad. Sci. U. S. A. **115**, E3333 (2018).

[18] D. Corradini, M. Rovere, and P. Gallo, J. Phys. Chem. B **115**, 14161 (2011).

[19] J. R. Errington and P. G. Debenedetti, Nature **409**, 318 (2001).

[20] M. C. Despretz, Ann. Chim. Phys. **70**, 49 (1839).

[21] M. C. Despretz, Ann. Chim. Phys. **73**, 296 (1840).

[22] L. F. Sedano, S. Blazquez, E. G. Noya, C. Vega, and J. Troncoso, J. Chem. Phys. **156**, 154502 (2022).

[23] F. Gámez, L. Sedano, S. Blazquez, J. Troncoso, and C. Vega, J. Mol. Liq. **377**, 121433 (2023).

[24] I. V. Leontyev and A. A. Stuchebrukhov, J. Chem. Theory Comput. **6**, 3153 (2010).

[25] I. V. Leontyev and A. A. Stuchebrukhov, J. Chem. Theory Comput. **6**, 1498 (2010).

[26] I. V. Leontyev and A. A. Stuchebrukhov, Phys. Chem. Chem. Phys. **13**, 2613 (2011).

[27] J. L. F. Abascal and C. Vega, J. Chem. Phys. **123**, 234505 (2005).

[28] C. Vega and J. L. F. Abascal, Phys. Chem. Chem. Phys. **13**, 19663 (2011).

[29] H. L. Pi, J. L. Aragones, C. Vega, E. G. Noya, J. L. Abascal, M. A. Gonzalez, and C. McBride, Mol. Phys. **107**, 365 (2009).

[30] G. L. Breton and L. Joly, J. Chem. Phys. **152**, 241102 (2020).

[31] V. M. Trejos, M. de Lucas, C. Vega, S. Blazquez, and F. Gámez, J. Chem. Phys. **159**, 224501 (2023).

[32] I. Zeron, J. L. F. Abascal, and C. Vega, J. Chem. Phys. **151**, 134504 (2019).

[33] S. Blazquez, M. M. Conde, J. L. F. Abascal, and C. Vega, J. Chem. Phys. **156**, 044505 (2022).

[34] S. Blazquez, I. M. Bourg, and C. Vega, J. Chem. Phys. **160**, 046101 (2024).

[35] M. Laliberte and W. E. Cooper, J. Chem. Eng. Data **49**, 1141 (2004).

[36] M. V. Kaulgud and W. K. Pokale, J. Chem. Soc., Faraday Trans. **91**, 999 (1995).