



You have downloaded a document from  
**RE-BUŚ**  
repository of the University of Silesia in Katowice

**Title:** Prediction of the speed of sound in ionic liquids as a function of pressure

**Author:** Bernadeta Jasiok, Eugene B. Postnikov, Ivan Yu. Pikalov, Mirosław Chorażewski

**Citation style:** Jasiok Bernadeta, Postnikov Eugene B., Pikalov Ivan Yu., Chorażewski Mirosław. (2022). Prediction of the speed of sound in ionic liquids as a function of pressure. "Journal of Molecular Liquids" (Vol. 363 (2022) art. no. 119792), doi 110.1016/j.molliq.2022.119792

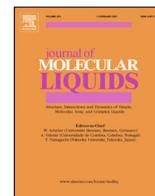


Uznanie autorstwa - Użycie niekomercyjne - Licencja ta pozwala na kopiowanie, zmienianie, remiksowanie, rozprowadzanie, przedstawienie i wykonywanie utworu jedynie w celach niekomercyjnych. Warunek ten nie obejmuje jednak utworów zależnych (mogą zostać objęte inną licencją).



Contents lists available at ScienceDirect

## Journal of Molecular Liquids

journal homepage: [www.elsevier.com/locate/molliq](http://www.elsevier.com/locate/molliq)

## Prediction of the speed of sound in ionic liquids as a function of pressure

Bernadeta Jasiok<sup>a,\*</sup>, Eugene B. Postnikov<sup>b,\*</sup>, Ivan Yu. Pikalov<sup>c</sup>, Mirosław Chorążewski<sup>a</sup><sup>a</sup> University of Silesia in Katowice, Institute of Chemistry, ul. 9 Szkolna, 40-006 Katowice, Poland<sup>b</sup> Theoretical Physics Department, Kursk State University, Radishcheva st., 33, Kursk 305000, Russia<sup>c</sup> Center for Information Systems Development and Data Analysis, Kursk State University, Radishcheva st., 33, Kursk 305000, Russia

## ARTICLE INFO

## Article history:

Received 16 April 2022

Revised 23 June 2022

Accepted 4 July 2022

Available online 5 July 2022

## Keywords:

High-pressure  
Speed of sound  
Ionic liquids  
FT-EoS

## ABSTRACT

In this work, we demonstrate the possibility of calculating the speed of sound of Ionic Liquids as a function of temperature and pressure using the fluctuation-based approach. The density, speed of sound, and heat capacity at atmospheric pressure are used for the calculations. The collected experimental data from the ILThermo database were used as input. The high-pressure speed of sound for nine ionic liquids was used to compare and analyze. Using the proposed method, the relative average absolute deviation is close to 0.85%.

© 2022 The Authors. Published by Elsevier B.V.

## 1. Introduction

Thermophysical properties of compressed liquids such as compressibilities, thermal expansivity, and heat capacities are quantities of great interest in several physics and physical chemistry fields. Thus many studies have been devoted to experimental measurements of the thermophysical properties of liquids and mixtures. Significantly, the effect of temperature and pressure on isothermal and isentropic compressibility, isobaric thermal expansivity, constant volume, constant pressure heat capacities, and speed of sound has been investigated by experiments for hundreds of molecular systems and mixtures. The state of any fluid is something engineering chemists often find it necessary to specify clearly. Such a specification for even the simplest fluid must include the amount of substance present, the pressure, and the temperature. The mathematical relationship that links them is the equation of state that remains the basis of thermodynamics. The equations of state were introduced to understand the physical background of liquids and use practical calculations instead of extensive direct measurements. The equations of state, and with them the thermoelastic coefficients, are the starting point for most thermodynamic problems in the field of application and engineering in connection with the molecular nature of the described systems, and the range of their applications is extensive, from

physical chemistry and fluid mechanics, through material engineering to nanotechnology.

However, current knowledge of equations of states in the meaning of practical usefulness indicates that the semi-empirical engineering approach is not entirely correct. It is worth noting that besides all the attempts and efforts devoted to the formulation of the versatile equation of state, none of the derived models, up to date, is efficient enough for the properties prediction of a wide range of liquids in a wide range of pressure changes, especially for novel working fluids with new and vastly improved properties.

On the other hand, complicated statistical mechanics apparatus leads to poor functionality with simultaneous mathematical nature complication of the model, which closes the possibility of broad, easy, and fast applicability for engineers. The interesting approach and the key to explaining these inconsistencies seem to work associating the easiness of equations of states from phenomenological thermodynamics, including the fluctuations phenomenon described by the statistical thermodynamics tools. It also increases the possibility of compiling versatile, fully predictive equations of state.

During this work, we decided to assess the predictive capability for the high-pressure physicochemical properties, primarily the speed of sound for Ionic Liquids (ILs), using an extension of the Fluctuating Equation of State. As has been known for a long time, ILs are liquid organic salts with different physicochemical properties and can therefore be used in various fields of science. For example, ILs can be used as electrolytes in lithium-ion batteries, organic synthesis, catalysis, solvent extraction, they are applied to various biochemical processes and many others [1–3].

\* Corresponding authors.

E-mail addresses: [bjasiok@us.edu.pl](mailto:bjasiok@us.edu.pl) (B. Jasiok), [postnikov@kursksu.ru](mailto:postnikov@kursksu.ru) (E.B. Postnikov).

It is known that ionic liquids have a complicated chemical structure and the nature of intermolecular interactions, so the speed of sound obtained from the experiment under the elevated pressure often does not meet the thermodynamic coherence criteria. Very often, there are relaxation effects in these liquids, which lead to the dispersion of the speed of sound, resulting in a non-thermodynamic speed of sound. This leads to obtaining experimental values not relevant for further thermodynamic modeling. It should be noted that the equation of state derived by us excludes the prediction of non-thermodynamic (i.e., incorrect) speed of sound. Thus, it also verifies the experimental data of speeds of sound.

The speed of sound as a function of a wide range of thermodynamic variables is necessary to determine the complete thermodynamic relations for liquids under high pressure and at elevated temperatures. Even though the speed of sound is not a thermodynamic property *per se*, it is closely related to other thermodynamic properties of a system [4–7]. Moreover, the pressure dependence of the speed of sound provides basic information about compressed liquids, both to investigate the nature of molecular and structural interactions and to obtain thermodynamic properties for applications in industrial processes. It is also essential for deriving and then validating many Equations of State of practical significance.

To date, molecular models belonging to the Statistical Association Fluid Theory (SAFT) family are the primary tools used in the literature to predict the speed of sound of compressed ILs over a wide range of pressures, and temperatures [8–11]. These models can exhibit remarkable accuracy in the comprehensive modeling of liquid properties. On the other hand, the prediction of the speed of sound is also possible using the recently proposed Daridon's method [7]. His approach uses a group contribution method to predict the speed of sound for high molecular weight *n*-alkanes and depict the correlation of speed of sound as a function of temperature and pressure for pure *n*-alkane series.

This work is an extension of the existing Fluctuation Equation of State, which makes it possible to predict the density, the isobaric thermal expansion coefficient, and isothermal compressibility [12–14] and, especially, the approach hypothesized and preliminarily tested for the case of simple hydrocarbons and their mixtures [15].

## 2. Materials and Method

### 2.1. Materials

In this study, we used as a primary source the data publicly available in the most comprehensive database of raw experimental measurements of the thermodynamic properties of ionic liquids, ILThermo (v.2.0). It was convenient to create two datasets for further processing for each thermodynamic quantity. The first dataset contains the information on the experiments themselves, i.e., links to information sources, information on the components, and the molar mass of the mixture. The second dataset contains the data of the results of the experiments used for the processing.

The procedure was implemented via the homemade PYTHON code for carrying out requests to the online database and saving the obtained data in Excel spreadsheets for further processing with MATLAB. The general principle of building such a program realization is described in detail elsewhere [16]. Thus, we shortly note only the basic principle of data obtaining.

In order to create the required datasets, it is necessary to request the server where the experiment data is stored, specifying the necessary parameters. In our case, we need to specify the number of mixture components equal to 1 (name on the form: Number

of mixture components, the parameter code is named as `ncmp`) and the property of interest (name on the form: Property, parameter, the parameter's code is `prp`). For example, one needs to execute the following program lines to get the speed of sound:

---

```
param = 'https://ilthermo.boulder.nist.gov/ILT2/ilsearch?
      cmp=&ncmp = 1&year=&auth=&keyw=&prp = HWGM'
response = requests.get(param)
data = response.json().get('res')
head = ['source_code', 'source_name', 'property',
        'phases', 'fluid_code', 'fluid_code2',
        'fluid_code3', 'col_point', 'fluid_name']
sos_exper = pd.DataFrame(data, columns = head)
```

---

The result is a dataset with fields containing the code of an experiment used in ILThermo (v.2.0), a reference to the experiment, the property, the phase, the component's code, several measurements, and chemical formulae of components. For further investigation, we only leave the measurements with the phase 'Liquid.' Then, we need to obtain the measurement data for each experiment. A list of experiment codes is generated.

---

```
sp_sos_exper_liquid = list(sos_exper_liquid
                          ['source_code'])
```

---

Then queries corresponding to the list of substances was carried out in a loop, and lists with the obtained data were formed:

---

```
for i in range(len(sp_sos_exper_liquid)):
code_exp = sp_sos_exper_liquid[i]
res = requests.get(main_url + 'ILT2/ilset?set=' +
                  code_exp)
```

---

Once the necessary lists had been created, the datasets were created and sorted respectively to the lists of unique codes for substances. For these goals, a list of ionic liquids, for which data on the speed of sound exist, was determined as follows:

---

```
sp_name_fl_unique = sos_exper_liquid
                  ['fluid_code'].unique()
```

---

and further requests refer to the unique codes, e.g.

---

```
https://ilthermo.boulder.nist.gov/ILT2/ilsearch?
      cmp=
      2-hydroxy-N-methylethanaminium
      formate&ncmp = 1&year=&auth=&keyw=&
      prp = xXKp
```

---

After getting all the speed of sound data, we need to get data for the density (and the isobaric heat capacity at the ambient condition in the case of those ionic liquids modeled with the FT-EoS-based approach at high pressures) the selected liquids. In order to do so, the same steps are followed, but with another required property, only in the first query for the experiments we have to substitute the name of the liquid in the loop as well.

## 2.2. Extraction of experimental data for further calculations

The set of data on the density, the heat capacity, and the speed of sound was downloaded from ILThermo with the PYTHON code operational principles, which are described above. In this particular case, some additional filters were applied: the check that the reported pressure does not exceed 102 kPa, i.e., corresponds to the measurements at ambient conditions, the phase state is strictly denoted as "Liquid", i.e., possible metastable liquids are excluded, strictly one-component compounds, the presence of a liquid's code in both lists (of the density and the speed of sound). Two hundred different ionic liquids were identified at this stage, and the raw data were downloaded.

Nevertheless, it should be pointed out that some of these datasets contain only a few (or even one unique) points and are not applicable for the goal of regression by a non-linear function within an interval of temperatures. Therefore, the secondary check procedures excluded those liquids for which data reported from less than four different temperatures reduced the number of different ionic liquids to 182 compounds.

However, there is still a problem with the coordination of datasets reported in different papers for the same ionic liquid and data uncertainty because some datasets look extremely scattered as functions of the temperature. For this reason, the following procedure was applied: since the change of values is not so drastic within the considered temperature intervals, the linear fitting of all data belonging to each particular ionic liquid was carried out (separately for the density and the speed of sound) and data points, which deviate from this fitting line more than 0.5 % in the relative average absolute deviation for the density and more than 0.2 % for the speed of sound, were excluded. Furthermore, an additional check that the kept values are series, which include not less than four elements (with possible repeating temperatures for the data from different sources), was carried out too to assure the possibility of the further fitting. After this procedure, 139 different ionic liquids remain on the list.

Finally, it should be pointed out that the model considered below operates with the thermodynamic qualities, i.e., it applies to the dispersionless region of ultrasound. For ionic liquids, it is known, see [17] that dispersion effects start to exhibit themselves from several hundreds of MHz. The datasets reported in ILThermo and analyzed in our work do not belong to this range; they explicitly stated their frequencies of ultrasound do not exceed 5 MHz; for those datasets where the frequency is not stated explicitly, the authors of the original works stated that the speed of sound measurements belong to the dispersionless, i.e., thermodynamic, conditions, for which our model is built.

## 2.3. Description of the procedure for predicting the speed of sound under elevated pressure

Among different mathematical models describing the dependence of the speed of sound as a function of the externally applied pressure [18], one can note that a formula expressing the speed of sound cubed can be fitted as a linear function of the pressure

$$c^3(P) = c_0^3 + \delta_s(P - P_0) \quad (1)$$

that was first described by Shoitov and Otpushchennikov [19] as an empiric observation. Here,  $c_0 = c(P_0)$  is the speed of sound at atmospheric pressure  $P_0$ , and  $\delta_s$  is a temperature-dependence constant, which should be defined. Below, in the section Discussion, we propose a physical picture that leads to such behavior.

For practically all organic liquids, Eq. 1 can be applied up to about 100–150 MPa and sometimes even for higher pressures when the liquid is very low compressibility. For larger pressures,

one needs to expand the pressure dependence that can be achieved, e.g., by adding a quadratic component, to obtain even better accuracy. It is, however, small enough compared to the linear part but is required when testing liquids above 200 MPa, as discussed in [20,21,15].

Within the frames of such a fitting procedure, depending on the pressure range, Eq. (1) can be considered as the first term of a Taylor expansion of the function  $c = c^3(P)$  along an isotherm

$$c^3 = c(P_0)^3 + \left(\frac{\partial c^3}{\partial P}\right)_{T,P=P_0} (P - P_0).$$

In the above equation, the partial derivative can be expressed as:

$$\left(\frac{\partial c^3}{\partial P}\right)_{T,P=P_0} = \left(\frac{\partial c^3}{\partial \rho}\right) \left(\frac{\partial \rho}{\partial P}\right)_{T,P=P_0} = \frac{3}{2} \rho_0 \kappa_T^0 c_0 \left(\frac{\partial(\rho \kappa_S)^{-1}}{\partial \rho}\right)_{T,P=P_0}. \quad (2)$$

Thus, to estimate the speed of sound at not extremely high pressures, one need to know the speed of sound and the isothermal compressibility at ambient pressures and, also, the partial derivative of the speed of sound squared  $c^2 = (\rho \kappa_S)^{-1}$  considered as a function of the density. The isothermal compressibility can be easily found via the standard thermodynamic equality

$$\kappa_T^0 = \frac{1}{\rho_0} \left( \frac{1}{c_0^2} + \frac{T \alpha_{P,0}^2}{C_{P,0}} \right) \quad (3)$$

when the speed of sound, the density, and the isobaric heat capacity at constant ambient pressure are known (note that in Eq. (3) and further, throughout the work, the mass-related quantities (e.g., the density and the specific heat capacity) are used); under these conditions, the isobaric coefficient of thermal expansion is the simple derivative

$$\alpha_{P,0} = \frac{1}{\rho_0} \left( \frac{\partial \rho_0}{\partial T} \right)_{P,0}. \quad (4)$$

Thus, the main question is in determining the derivative  $(\partial(\rho \kappa_S)^{-1}/\partial \rho)_T$  without the usage of the high-pressure data. It is known [22,23] that considering the speed of sound as a pure function of the density is not enough for this goal because of the different values of the respective derivative along the isothermal and isobaric paths. On the other hand, the adiabatic reduced fluctuation parameter

$$v_s = \frac{M}{RT} \frac{1}{\rho \kappa_S}, \quad (5)$$

which is connected with the ratio of pressure fluctuations [24]

$$\langle (\Delta P)^2 \rangle = -RT \left( \frac{\partial P}{\partial V} \right)_S = \frac{RT}{M} \left( \frac{\partial P}{\partial \rho} \right)_S \rho^2.$$

in the actual medium and in the hypothetical case where a substance acts as an ideal gas for the same pressure–temperature–volume (PVT) parameters has the desired invariant property as it has been shown in the work [15].

It can be expressed as a function of the density only

$$v_s = \frac{M}{R} \frac{c^2}{T} \equiv \frac{M}{RT} \frac{1}{\rho \kappa_S} = \Lambda \rho^\lambda, \quad (6)$$

and this power-law scaling fulfils allows considering derivatives with respect to the density independently of the fixed either the pressure or the temperature.

This implies that

$$\frac{dv_s}{d\rho} = \lambda \frac{M}{RT} \frac{c^2}{\rho}.$$

Respectively, along an isotherm, i.e., for  $T = \text{const}$ , where  $M/(RT)$  does not change and can be omitted,

$$\left(\frac{\partial(c^2)^{\frac{3}{2}}}{\partial\rho}\right)_{T,P=P_0} = \frac{3}{2}c_0\left(\frac{\partial c^2}{\partial\rho}\right)_{T,P=P_0} = \frac{3}{2}\lambda\frac{c_0^3}{\rho_0}$$

and the final expression, which will be applied to predict the speed of sound, takes the form

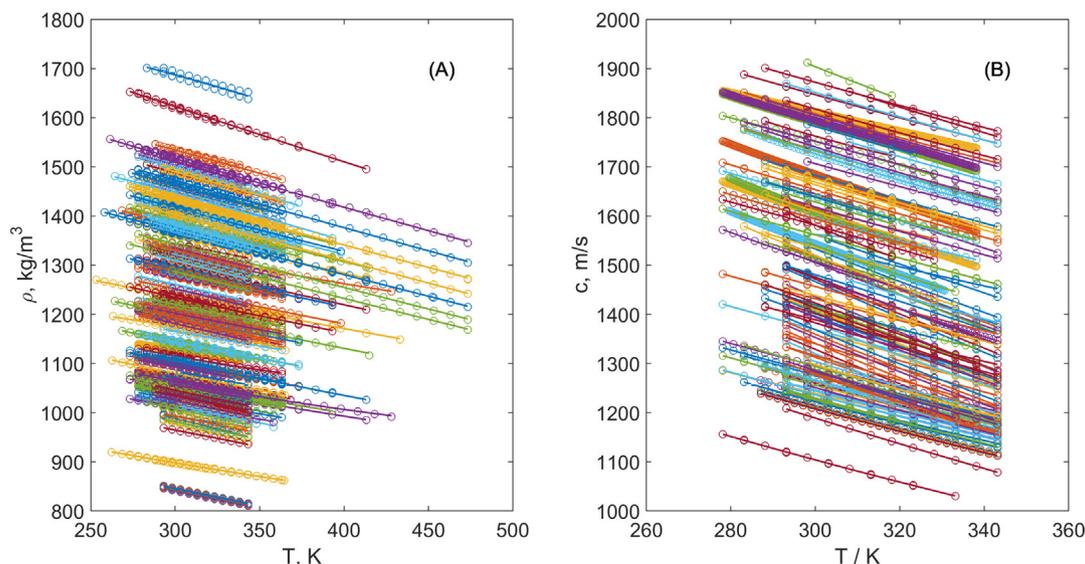
$$c = c_0 \left[ 1 + \frac{3}{2} \kappa_T^0 \lambda (P - P_0) \right]^{\frac{1}{3}}. \quad (7)$$

### 3. Results

The principal studies aimed an investigation the possibility of application of the approach based on the assumption of the linearity of the pressure dependence of the speed of sound cubed (1) and the power-law scaling of the reduced pressure fluctuations (6) as the premise for searching the principal control parameter of this method, can be subdivided into two particular subtasks. The first one is the test of the validity of Eq. (6) at ambient pressure. Due to a large number of available experimental data, we analyze the universality of such dependence and its power-law parameter. As the next step, we apply the revealed control quantities to the direct test of the predictive capacity of the expression (7).

#### 3.1. Using experimental data under ambient pressure: a test of the power-law scaling

The data on the density and the speed of sound filtered as described in subsection 2.2, were polynomially fitted as functions of the temperature: if a dataset is short (less than five data points), the linear fit was applied; otherwise – the quadratic one; for the sake of numerical stability, the centering and scaling of the data was applied as an intermediate step during the regression procedure. The resulting approximations of the data and the respective data themselves are shown in Fig. 1. One can see that the fitting functions (lines) reproduce the course of data (circles) sufficiently accurately.



**Fig. 1.** The temperature dependencies of the density (A) and the speed of sound (B) at ambient pressure for 140 ionic liquids (each liquid is marked by a different color, see the complete list of ILS in Supplementary Information). Circles denote experimental data, and lines show linear or quadratic fits in the least mean squares sense.

The data were filtered in such a way that we used them to check the fulfillment of the power-law dependence on the density, Eq. (6).

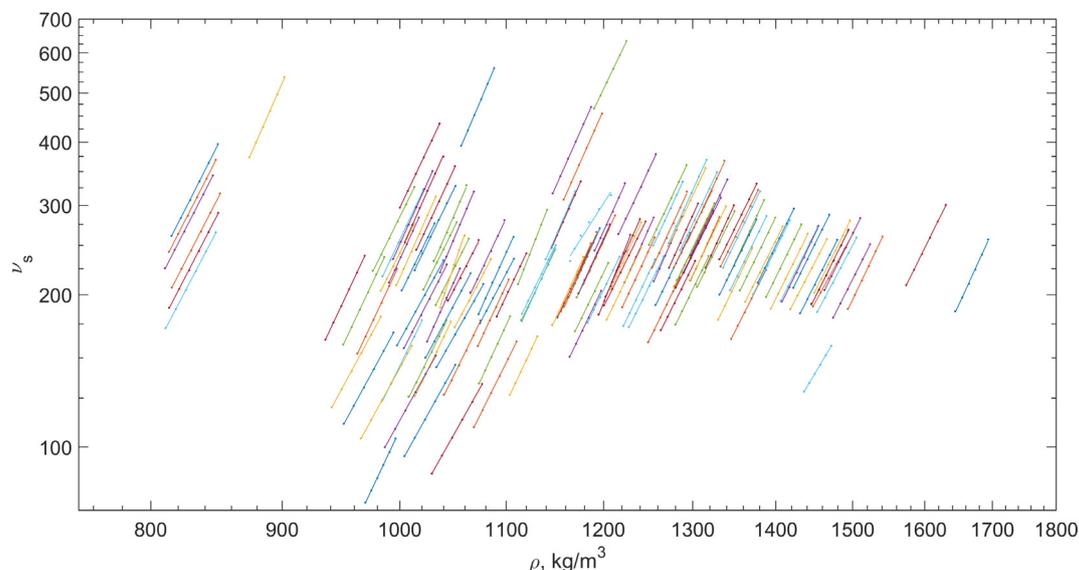
For this purpose, the equispaced sets of the density and the speed of sound values were calculated with the polynomial approximations described above from  $T = 293.15$  K to  $T = 343.15$  K (this interval covers the majority of existing experimental measurements, see Fig. 1(B)), with the step 10 K. Fig. 2 represents the respective plots, where the experimental-based quantities are shown as dot. In double logarithmic coordinates used for demonstrability, one can see that they follow straight lines

$$\ln(v_s) = \ln(\Lambda) + \lambda \ln(\rho) \quad (8)$$

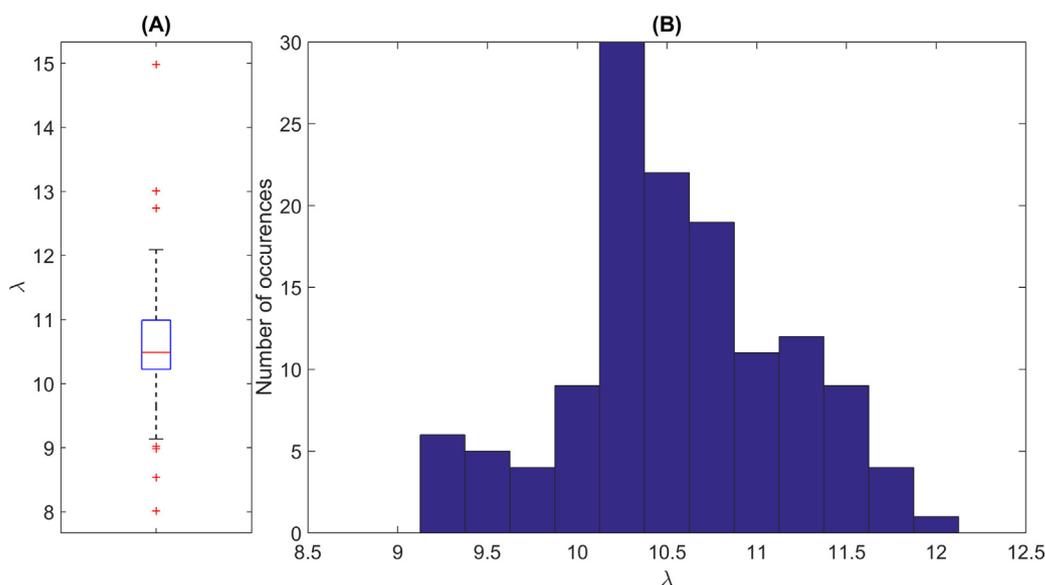
as expected from Eq. (6).

The linear regression (shown as a line for each dataset in Fig. 2) gives the slope of such a line, i.e., the desired parameter  $\lambda$ . Even by a naked eye, it is visible that all slopes are very similar. The descriptive statistics confirm this; see the box-and-whiskers plot, Fig. 3(A), which indicates that they are concentrated within a rather narrow range. At the same time, there are several outliers denoted as red pluses, a few already, 7 of 139. This liquids are: N-methyl-2-oxopyrrolidinium formate, trimethylammonium hydrogen sulfate, 2-hydroxy-N,N,N-trimethylethanaminium (S)-2-hydroxypropanoate, N-(2-hydroxyethyl) benzenaminium propionate, 1-hexyl-3-methylimidazolium thiocyanate, 1-ethyl-1-methylpyrrolidinium ethyl sulfate, and 3-hexyl-1-methyl-1H-imidazolium bromide. A more detailed investigation of the respective experimental data revealed that these substances are characterized by a limited number of experimental data, which still have a rather irregular scattering with high uncertainty around the fitting polynomials. Therefore, they should be excluded from consideration from the statistical point of view as requiring additional experimental measurements aimed at the more reliable determination of their thermodynamic properties.

Fig. 3(B) demonstrates the distribution histogram for the rest of 132 ionic liquids, which are accepted as based on reliable data; bins of the histogram are centered in points from 9.25 to 12 with equal widths of 0.25. It can be stated that the range of change of  $\lambda$  for ionic liquids is quite narrow. The distribution has a clear maximum, the model is  $\lambda = 9.14$ ; the mean value is  $\lambda = 10.55$ , close to



**Fig. 2.** The dependence of dimensionless reduced pressure fluctuations on the density in 140 ionic liquids (the color coding is the same as in Fig. 1); dots are values calculated with the fits of experimental data, and straight lines are the linear fits of the latter considered in the double logarithmic coordinates.



**Fig. 3.** A standard box-and-whiskers plot describing statistics of the parameter  $\lambda$  for all 139 explored ionic liquids (A) and the distribution of  $\lambda$  values with excluded outliers (B).

the median equal to  $\lambda = 10.50$ ; the standard deviation is equal to  $\text{std}(\lambda) = 0.61$ .

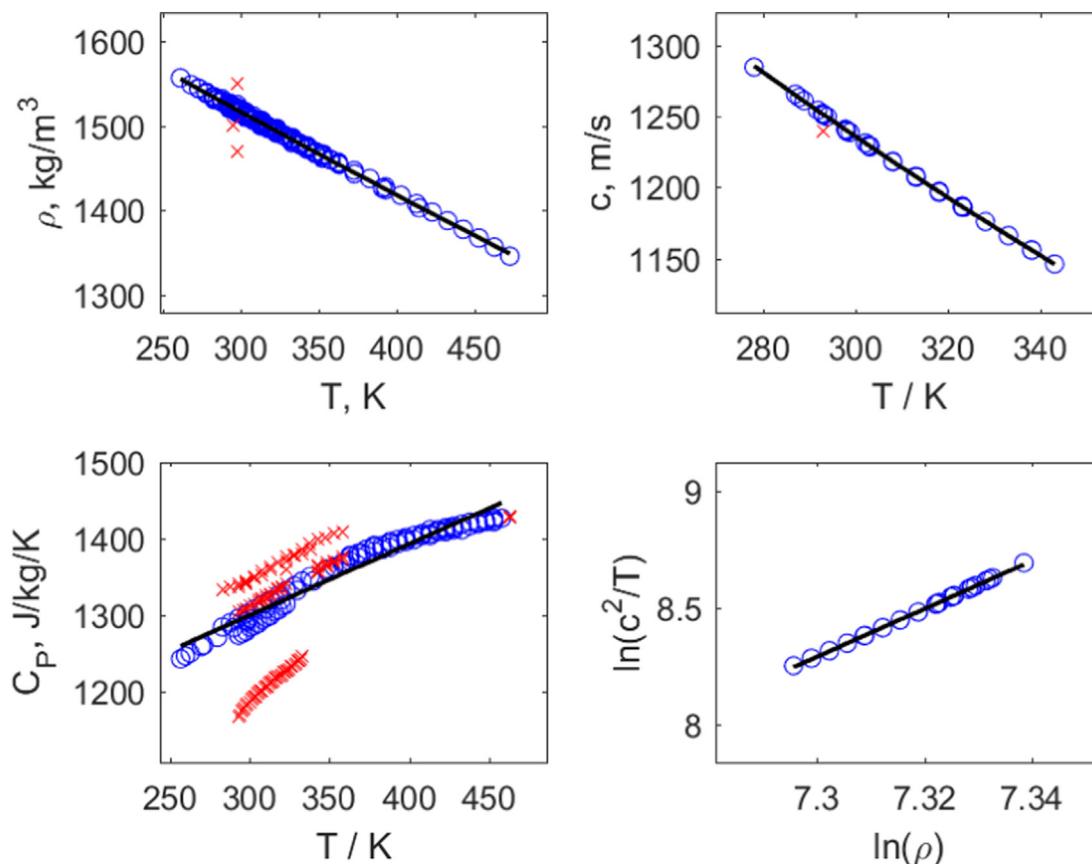
### 3.2. The results of calculations of the speed of sound in the high-pressure range

Usually, the experimental data for ILs, the density, and speed of sound at atmospheric pressure, are much more common than experimental data for the speed of sound in the high-pressure range. Our work focused only on experimental data from the ILThermo database intended to not refer to any data either calculated or predicted by any model approaches that are not observed in real measurements. Based on this, the high-pressure values of speed of sound for nine ILs were collected. The speed of sound of ILs was predicted and assessed using 589 data points using Eq.

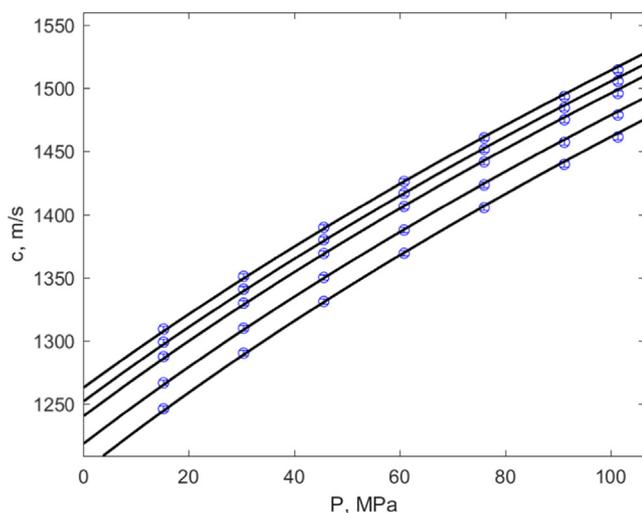
(7) with parameters found using only the fitting experimental data measured at ambient pressure.

Fig. 4 shows an example of such data preprocessing for 1-ethyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide. It is worth noting that such a filtering procedure is already necessary since it is visible that the experimental data are already very scattered, especially on the density, speed of sound, and isobaric heat capacity. In our approach, large outliers, marked as red 'x,' some of which are beyond any reasonable experimental uncertainty, were excluded from the trend during the evaluation procedure. The rest of the data were used to calculate parameters of Eq. (7) and the speed of sound itself with this formula.

Fig. 5 presents a comparison of the pressure dependence of the speed of sound of 1-ethyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide between the values calculated via this route and collected experimental results. We obtained one of the better



**Fig. 4.** The density, speed of sound, heat capacity as a function of temperature, and the natural logarithm of the square of the speed of sound to temperature as a function of the natural logarithm of density for 1-ethyl-3-methylimidazolium bis((trifluoromethyl) sulfonyl)imide.



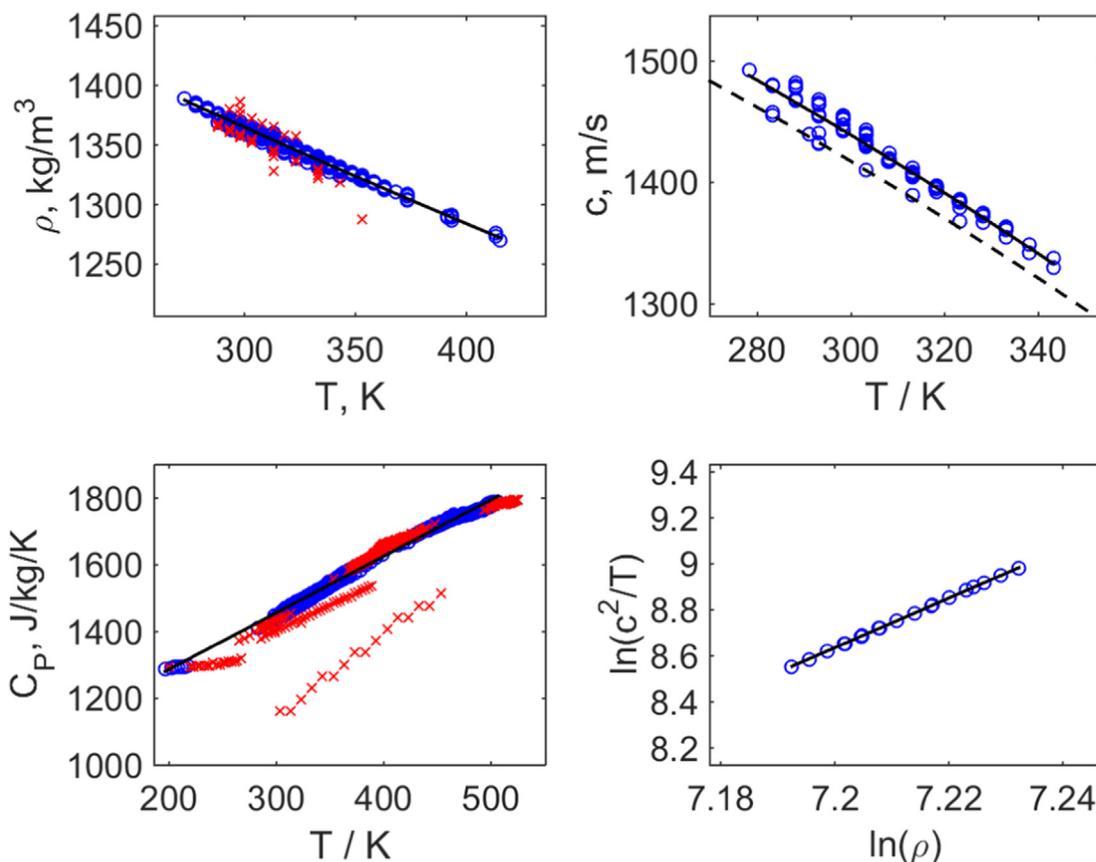
**Fig. 5.** A comparison of the pressure dependence of the speed of sound between FT-EoS and collected experimental results for 1-ethyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide for (288, 292, 298, 308 and 318) K from up to down.

results for this IL, where the average absolute deviations (AAD) were only 0.1 %.

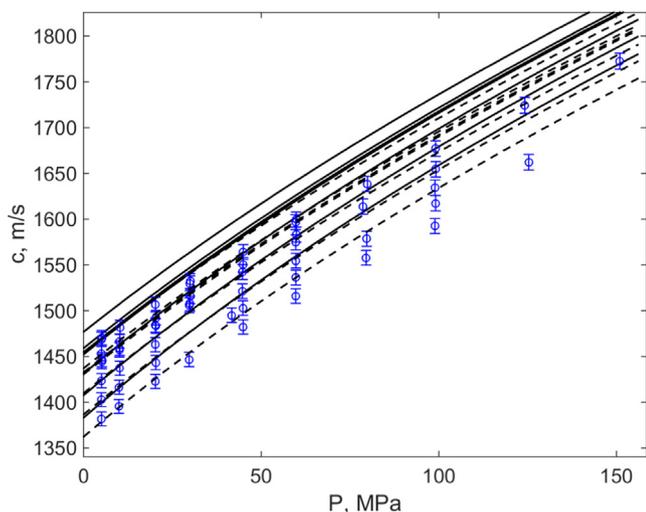
At the same time, it should be stressed that such a perfect prediction is achieved due to the regularity and consistency of the reference data used for the determination of the parameters. Our second example, 1-butyl-3-methylimidazolium hexafluorophosphate illustrates this caveat. Fig. 6 indicates that the data provided

by different authors are significantly inconsistent that influence the prediction quality even after removing the most deviating ones. In this respect, the uncertainty in the pressure and the speed of sound is most influential for two reasons: 1) the term  $1/(\rho_0 k_T^0)$  is leading in Eq. 3 and, respectively, influences the slope of the speed of sound cubed as a function of the pressure; 2) deviations in the speed of sound  $c_0$  directly lead to the displacements in the whole set of the resulting  $C(P)$  as it directly follows from Eq. (7). The latter fact is the most obvious: among the data  $c_0(T)$  shown in Fig. 6, one can see a sequence of points, which follow the dashed line shifted relatively to other data following the solid line. The fact is that values at ambient pressure correspond to measurements reported for high pressures. As a result, the predicted values obtained using the most consistent regularities in the data at ambient pressure give the relative average absolute deviations 2.5 % from the experimentally reported values. They are shown in Fig. 7 as solid lines and circles, respectively. On the other hand, if to refer to the initial values of the speed of sound, which are 1.5 % less than the other (the dashed line in Fig. 6), the deviation reduces down to 0.94 %, see the dashed curves in Fig. 7. The difference in the slope still kept even, in this case, originates from uncertainty in the density values forming rather a wide stripe than a line in Fig. 6.

The obtained results for all collected ILs with model characteristic  $\lambda$ , average absolute deviations (AAD), and uncertainties of experimental data  $unstr_{exp}$  are presented in Table 1. By applying our method, the agreement, well-coordinated with the possibilities of actual experimental methods, is observed between experimental and predicted high-pressure speed of sound data for all collected ILs from the ILThermo database. An overall relative average absolute deviation (RAAD) is close to 0.85 %.



**Fig. 6.** The density, speed of sound, heat capacity as a function of temperature, and the natural logarithm of the square of the speed of sound to temperature as a function of the natural logarithm of density for 1-butyl-3-methylimidazolium hexafluorophosphate.



**Fig. 7.** A comparison of the pressure dependence of the speed of sound between FT-EoS and collected experimental results for 1-butyl-3-methylimidazolium hexafluorophosphate for (283, 291, 293, 294, 303, 313 and 323) K from up to down.

#### 4. Discussion

The possibility of an approximate prediction of the speed of sound in ionic liquids under elevated pressures and on the data obtained at ambient pressure has premises in two kinds of scaling dependencies: between the speed of sound and the pressure, and

**Table 1**  
Obtained results for all collected ILs from ILThermo database with model characteristic  $\lambda$ , average absolute deviations (AAD) and uncertainties of experimental data  $unstr_{exp}$ . The maximal pressures are either 100 MPa or 150 MPa.

IL name	$\lambda$	AAD [%]	$unstr_{exp}$ [%]
1-butyl-3-methylimidazolium dicyanamide	10.2	1.2	1.4
1-butyl-3-methylimidazolium tetrafluoroborate	10.6	1.2	0.43
1-butyl-3-methylimidazolium hexafluorophosphate	10.8	2.4	0.53
1-butyl-3-methylimidazolium hexafluorophosphate	10.8	0.94*	0.53
1-butyl-3-methylimidazolium trifluoromethanesulfonate	10.4	1.1	1.4
1-ethyl-3-methylimidazolium bis((trifluoromethyl) sulfonyl)imide	10.2	0.1	0.15
1-butyl-3-methylimidazolium bis((trifluoromethyl) sulfonyl)imide	10.4	0.16	0.23
1-butyl-1-methylpyrrolidinium bis((trifluoromethyl) sulfonyl)imide	10.6	0.56	1.1
1-methyl-3-pentylimidazolium bis((trifluoromethyl) sulfonyl)imide	10.5	0.43	0.2
1-hexyl-3-methylimidazolium bis((trifluoromethyl) sulfonyl)imide	10.4	0.076	0.47

\* When the speeds of sound at ambient pressure are coordinated with the values provided in the same source as for the high-pressure data, their relative difference with the data obtained by averaging over all available sources is about 1.5 %.

between the thermodynamic fluctuations of thermodynamic quantities and the density.

The first kind of scaling is dated back to the empiric Rao rule, which was initially detected for the ambient pressure data [25] in the form

$$\frac{c^{1/3}}{\rho} = K \quad (9)$$

where  $K$  is a compound-specific constant. Later, the similar expression

$$\frac{c^{1/3}}{\rho} = K' \quad (10)$$

was found [26] for the dependencies measured along isotherms. However, it should be pointed out that the parameter  $K'$  included in Eq. (10) does not coincide with  $K$  included in Eq. (9), making impossible the direct transfer of data from the isobaric to the isothermal path [22,23]. At the same time, the isothermal functional form (10) has a more substantial background from the molecular point of view [27,28]. Note that it can be rewritten as

$$c^3 = K' \rho^9, \quad (11)$$

whence one needs to consider the relation of the 9th degree of the density along an isotherm to the pressure applied. Nevertheless, there is no universal power-law dependence valid for all kinds of liquids and pressure range [29] although it can be found for very high pressure. Recently, this fact was explained within the frame of the two-state model [30], which considers the structural difference between the loosely and closely packed structure of a liquid under moderate and high pressures, respectively.

At the same time, there is a more accurate *adiabatic* equation of state first proposed by Brinkley Jr & Kirkwood [31] and well-supported further experimental investigations. It has the form

$$P - P_0 = B(S) \left[ \left( \frac{\rho}{\rho_0} \right)^\gamma - 1 \right], \quad (12)$$

as a direct generalization of the adiabatic equation of state of gases but here  $\gamma$  is not the ratio of heat capacities but some empiric coefficient.

It is well-known that the entropy of liquid changes more slowly along isotherms than along the ambient pressure isobar. As a consequence, the expression similar to Eq. (12) is sometimes used for the isothermal change of the density (Murnaghan's equation); in particular, Chueh & Prausnitz [32] considered the dependence

$$\left( \frac{\rho}{\rho_0} \right)^9 = 1 + 9\kappa_T^0 (P - P_0), \quad (13)$$

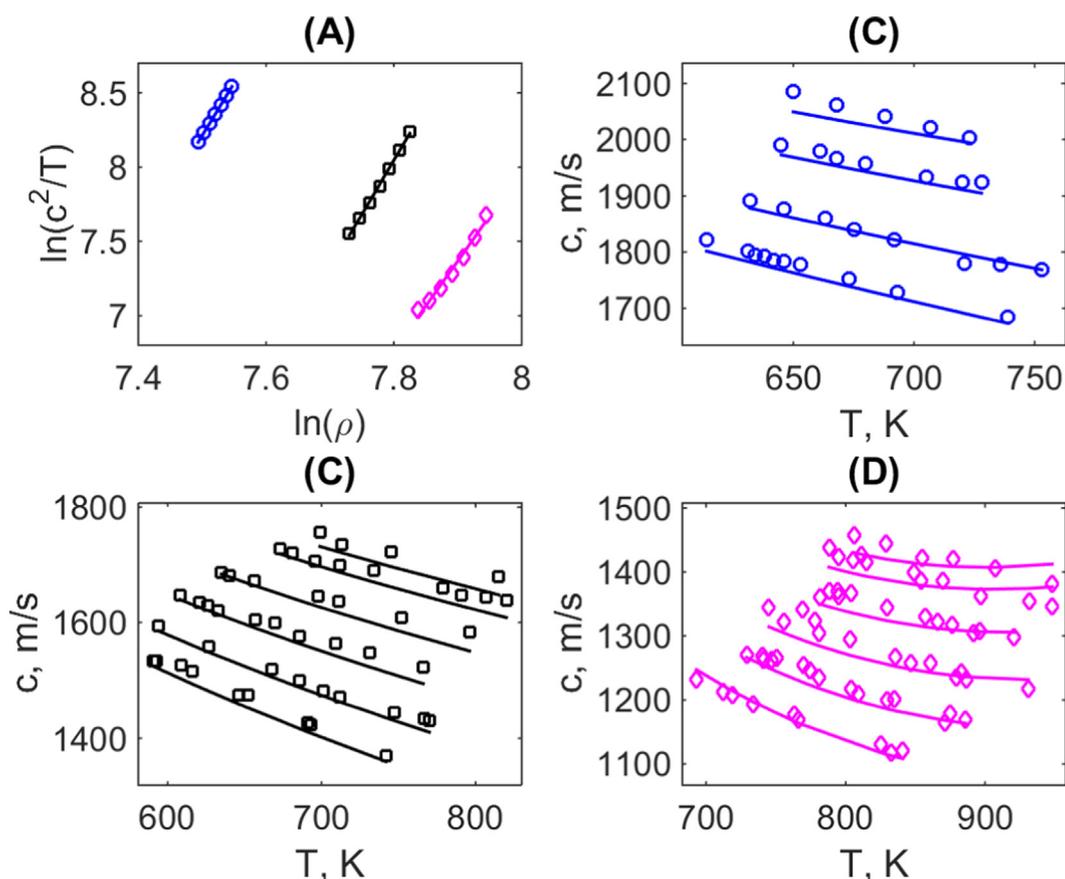
where  $\kappa_T^0$  is the isothermal compressibility at ambient (or saturation) pressure for several organic liquids.

The same form as Eq. (13) with  $\gamma = 9 \div 11$  has also been actively explored more recently [33–35] within the concept of the density scaling regime of different compressed liquids including ionic ones. The substitution of Eq. (13) in Eq. (11) gives

$$c^3 = K' \rho_0^9 [1 + 9\kappa_T^0 (P - P_0)], \quad (14)$$

i.e. the same dependence of the speed of sound cubed, which we used as the principal assumption in our derivation; here  $K' \rho_0^9 = c_0^3$  but the coefficient  $K'$  itself is still indefinite.

At the same time, it is worthy that the more accurate is the isobaric equation rather than the isothermal one. Thus, we need to



**Fig. 8.** (A) The plot demonstrating the density scaling of the variable part of the reduced pressure analogues to Fig. 2  $\text{NaNO}_3$  (circles),  $\text{RbNO}_3$  (squares), and  $\text{CsNO}_3$  (diamonds); comparisons of the predicted and experimental data: (B) for  $\text{NaNO}_3$  along isobars (18.6, 100.0, 200.0, and 283.0) MPa ordered from down to up; (C) for  $\text{RbNO}_3$  along isobars (25.2, 84.4, 153.0, 227.8, 304.2, and 343.8) MPa ordered down to up; (D) for  $\text{CsNO}_3$  along isobars (23.6, 85.4, 153.1, 227.7, 304.2, and 346.4) MPa ordered from down to up.

operate with relations that are less sensitive to the change in thermodynamic path. In this sense, it is crucial that the sound spread is an adiabatic (isentropic) process and fluctuations of the pressure, expressed via the speed of sound Eq. 2, and the fluctuations of entropy are independent [24]. Thus, when we used the fitting of the reduced pressure fluctuations as a power-law function of the density along an isobaric path (where the entropy changes significantly), we are entitled to transfer the obtained power-law index to the isothermal path. This is the main advantage of our approach, based on the fundamental statistical physics, over Rao's (or Rao-Carnevale-Litovitz's) approach, which lacks such invariance.

Finally, as a short additional test, we applied our approach to predict the speed of sound under pressure for molten salts, which, as ionic liquids, belong to the class of substances with strong ionic interaction but exist in liquid state in a much more high range of temperatures. It is worth noting that the number of high-pressure speed of sound data for molten salts is extremely scarce. Thus, as an example for this case study we used high-pressure experimental data for three molten salts, namely i) sodium nitrate,  $\text{NaNO}_3$ , ii) rubidium nitrate,  $\text{RbNO}_3$ , and iii) cesium nitrate,  $\text{CsNO}_3$  reported in the work [36]. The full set of thermodynamic data measured at atmospheric pressure was taken from Refs. [37–40]. The obtained results for these compounds are shown in Fig. 8 as a comparison of the predicted (lines) and the experimental (markers) values.

The primary question, which should be answered as giving the principal criterion of validity of the model (7), is whether the reduced pressure fluctuations scale as a power-law function of the density. Fig. 8 positively answers this question: for  $\text{NaNO}_3$  and  $\text{RbNO}_3$  linearity of the fit looks perfect, the situation  $\text{CsNO}_3$  is less accurate but still acceptable. Note that the original experimental data for this molten salt are also more scattered compared to two others that may originate from complications with the measurements at higher temperatures. The values of the scaling parameter  $\lambda$  are equal to 7.12, 7.24, and 6.04 for  $\text{NaNO}_3$ ,  $\text{RbNO}_3$ , and  $\text{CsNO}_3$ , respectively. These values are less than for room-temperature ionic liquids shown in Fig. 3. This fact is in line with the observation that the classic isobaric Rao's parameter is less than most molecular liquids, as discussed in Ref. [37].

However, these diminished values of the scaling parameter do not prevent the possibility of predicting the speed of sound in molten salts at elevated pressures, even up to the higher pressures in comparison with room-temperature ionic liquids, as one can see in Figs. 8 (B)–(D). Note that the data are represented along isobars correspondingly to the procedure of measurements and raw experimental data reported in Ref. [36]. The AADs for  $\text{NaNO}_3$ ,  $\text{RbNO}_3$ , and  $\text{CsNO}_3$  are 0.77 %, 1.02 %, and 1.20 %, respectively. We would like to highlight that uncertainty of experimental data themselves is about 1 %. Therefore the predictions are in the range of uncertainty of the measured values (also note a visible scattering of the latter in Figs. 8 (B)–(D)).

Thus, we can conclude that the strong ionic interactions and high temperatures do not hinder the use of the proposed methods, as demonstrated by its application to molten salts.

## 5. Conclusions

In light of this work, one can conclude that the proposed method can truly predict the speed of sound of ILs under high-pressure conditions with high accuracy. The density, speed of sound, and isobaric heat capacity at atmospheric pressure were used for the calculations. The modifications and modeling of the equation of state based on the fluctuation theory for first density, isobaric thermal expansion coefficient, isothermal compressibility, and second speed of sound are the strong fundamentals of useful

equations of state for the prediction various thermophysical properties. It is worth noting that this proposed model of fluctuation equation of state based on the knowledge of simple physicochemical properties obtained from an uncomplicated experiment at atmospheric pressure correctly predicts the thermodynamic properties of compressed liquid phase without prior knowledge of any properties of the tested object under elevated pressure. At the same time, we need to attract attention to the fact that such an approach requires establishing the consistency of the respective experimental data because the predictive capacity of the model at high pressures is heavily dependent on the accuracy of inputs used for the calculation of its parameters. This mathematical model will be, in the future, the starting point for the construction of relatively easy calculation tools for full and proper thermodynamic descriptions of compressed liquids.

## 6. Author Contributions

Bernadeta Jasiok – Conceptualization, Methodology, Validation, Formal analysis, Investigation, Resources, Data Curation, Writing - Original Draft, Writing - Review & Editing, Visualization, Project administration; Eugene B. Postnikov – Conceptualization, Methodology, Software, Validation, Formal analysis, Investigation, Resources, Data Curation, Writing - Original Draft, Writing - Review & Editing, Visualization, Supervision, Project administration; Ivan Yu. Pikalov – Software, Resources, Writing - Review & Editing; Mirosław Chorążewski – Conceptualization, Validation, Investigation, Resources, Writing - Review & Editing, Supervision, Funding acquisition.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Acknowledgements

This work was supported by a grant from the National Science Centre (Poland) Decision No. 2016/23/B/ST8/02968 and PIK – Program for new interdisciplinary elements of education at the doctoral level for a field of chemistry, POWR.03.02.00–00-1010/17 (Poland).

## Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.molliq.2022.119792>.

## References

- [1] D.D. Patel, J.-M. Lee, Applications of ionic liquids, *Chem. Rec.* 12 (2012) 329–355, <https://doi.org/10.1002/tcr.201100036>.
- [2] A.J. Greer, J. Jacquemin, C. Hardacre, Industrial applications of ionic liquids, *Molecules* 25 (2020) 5207, <https://doi.org/10.3390/molecules25215207>.
- [3] A. Ray, B. Saruhan, Application of ionic liquids for batteries and supercapacitors, *Materials* 14 (2021) 2942, <https://doi.org/10.3390/ma14112942>.
- [4] A. Queimada, J. Coutinho, I. Marrucho, J.-L. Daridon, Corresponding-states modeling of the speed of sound of long-chain hydrocarbons, *Int. J. Thermophys.* 27 (4) (2006) 1095–1109.
- [5] K.-J. Wu, Q.-L. Chen, C.-H. He, Speed of sound of ionic liquids: Database, estimation, and its application for thermal conductivity prediction, *AIChE J.* 60 (3) (2014) 1120–1131.
- [6] J. Skowronek, M. Dzida, E. Zorębski, M. Chorążewski, S. Jeżak, M. Źarska, M. Zorębski, P. Goodrich, J. Jacquemin, High pressure speed of sound and related thermodynamic properties of 1-alkyl-3-methylimidazolium bis

- [(trifluoromethyl) sulfonyl] imides (from 1-propyl- to 1-hexyl-), *Journal of Chemical & Engineering Data* 61 (11) (2016) 3794–3805.
- [7] J.-L. Daridon, Predicting and correlating speed of sound in long-chain alkanes at high pressure, *Int. J. Thermophys.* 43 (5) (2022) 1–32.
- [8] J. Pilarz, I. Polishuk, M. Chorążewski, Prediction of sound velocity for selected ionic liquids using a multilayer feed-forward neural network, *J. Mol. Liq.* 347 (2022) 118376, <https://doi.org/10.1016/j.molliq.2021.118376>.
- [9] J. Pilarz, J. Feder-Kubis, V.V. Melent'ev, O.S. Ryshkova, V.I. Korotkovskii, A.K. Radchenko, E.B. Postnikov, M. Chorążewski, I. Polishuk, Speeds of sound in ionic liquids under elevated pressures. new experimental data and cp-pc-saft modelling, *J. Mol. Liq.* 303 (2020) 112669, <https://doi.org/10.1016/j.molliq.2020.112669>.
- [10] Y. Xu, R. Shahriari, Prediction of second order derivative thermodynamic properties of ionic liquids using saft-vr morse equation of state, *Fluid Phase Equilib.* 549 (2021) 113204, <https://doi.org/10.1016/j.fluid.2021.113204>.
- [11] F. Bakhtazma, F. Alavi, Second-order thermodynamic derivative properties of ionic liquids from epc-saft: the effect of partial ionic dissociation, *Industr. Eng. Chem. Res.* 58 (2019) 22408–22417, <https://doi.org/10.1021/acs.iecr.9b05593>.
- [12] M. Chorążewski, E.B. Postnikov, B. Jasiok, Y.V. Nedyalkov, J. Jacquemin, A fluctuation equation of state for prediction of high-pressure densities of ionic liquids, *Scientific Reports* 7 (2017) 1–9, <https://doi.org/10.1038/s41598-017-06225-9>.
- [13] B. Jasiok, E.B. Postnikov, M. Chorążewski, The prediction of high-pressure densities of different fuels using fluctuation theory-based tait-like equation of state, *Fuel* 219 (2018) 176–181, <https://doi.org/10.1016/j.fuel.2018.01.091>.
- [14] B. Jasiok, A.R. Lowe, E.B. Postnikov, J. Feder-Kubis, M. Chorążewski, High-pressure densities of industrial lubricants and complex oils predicted by the fluctuation theory-based equation of state, *Industrial & Engineering Chemistry Research* 57 (34) (2018) 11797–11803, <https://doi.org/10.1021/acs.iecr.8b01542>.
- [15] E.B. Postnikov, B. Jasiok, V.V. Melent'ev, O.S. Ryshkova, V.I. Korotkovskii, A.K. Radchenko, A.R. Lowe, M. Chorążewski, Prediction of high pressure properties of complex mixtures without knowledge of their composition as a problem of thermodynamic linear analysis, *J. Mol. Liq.* 310 (2020) 113016, <https://doi.org/10.1016/j.molliq.2020.113016>.
- [16] E.B. Postnikov, I.T. Pikalov, M. Chorążewski, Thermal conductivity of ionic liquids: recent challenges facing theory and experiment, *Journal of Solution Chemistry*, submitted.
- [17] M. Dzida, E. Zorębski, M. Zorębski, M. Żarska, M. Geppert-Rybczyńska, M. Chorążewski, J. Jacquemin, I. Cibulka, Speed of Sound and Ultrasound Absorption in Ionic Liquids, *Chemical Reviews* 117 (2017) 3883–3929, <https://doi.org/10.1021/acs.chemrev.5b00733>.
- [18] B.A. Oakley, D. Hanna, M. Shillor, G. Barber, Ultrasonic parameters as a function of absolute hydrostatic pressure. II. Mathematical models of the speed of sound in organic liquids, *J. Phys. Chem. Ref. Data* 32 (2003) 1535–1544, <https://doi.org/10.1063/1.1555589>.
- [19] Y.S. Shoitov, N. Otpushchennikov, Pressure dependence of the speed of sound in liquids, *Soviet Physics Journal* 11 (12) (1972) 129–130.
- [20] A.R. Lowe, B. Jasiok, V.V. Melent'ev, O.S. Ryshkova, V.I. Korotkovskii, A.K. Radchenko, E.B. Postnikov, M. Spinnler, U. Ashurova, J. Safarov, E. Hassel, M. Chorążewski, High-temperature and high-pressure thermophysical property measurements and thermodynamic modelling of an international oil standard: Ravenol diesel rail injector calibration fluid, *Fuel Process. Technol.* 199 (2020) 106220, <https://doi.org/10.1016/j.fuproc.2019.106220>.
- [21] V.V. Melent'ev, M.F. Bolotnikov, Y.A. Neruchev, Speeds of sound, densities, and isentropic compressibilities of 1-iodohexane at temperatures from (293.15 to 413.15) K and pressures up to 200 MPa, *Journal of Chemical & Engineering Data* 50 (4) (2005) 1357–1360, [doi:10.1021/je050069s](https://doi.org/10.1021/je050069s).
- [22] B.B. Kudryavtsev, G.A. Samgina, Use of ultrasonic measurements in the study of molecular interactions in liquids, *Soviet Physics Journal* 9 (1966) 5–8, <https://doi.org/10.1007/BF00818478>.
- [23] R.A. Aziz, D.H. Bowman, C.C. Lim, An examination of the relationship between sound velocity and density in liquids, *Can. J. Phys.* 50 (1972) 646–654, <https://doi.org/10.1139/p72-089>.
- [24] L.D. Landau, E.M. Lifshitz, *Statistical Physics*, Vol. 5, Elsevier, 2013.
- [25] M.R. Rao, Velocity of sound in liquids and chemical constitution, *J. Chem. Phys.* 9 (1941) 682–685, <https://doi.org/10.1063/1.1750976>.
- [26] E.H. Carnevale, T.A. Litovitz, Pressure dependence of sound propagation in the primary alcohols, *J. Acoust. Soc. Am.* 27 (1955) 547–550, <https://doi.org/10.1121/1.1907959>.
- [27] R.V.G. Rao, B.S.M. Rao, Variation of sound velocity through liquids with pressure, *Trans. Faraday Soc.* 62 (1966) 2704–2708, <https://doi.org/10.1039/TF9666202704>.
- [28] W. Schaaffs, Molekularakustische Ableitung einer Zustandsgleichung für Flüssigkeiten bei hohen Drucken, *Acustica* 30 (1974) 275–280.
- [29] J.R. Macdonald, Some simple isothermal equations of state, *Rev. Mod. Phys.* 38 (1966) 669–679, <https://doi.org/10.1103/RevModPhys.38.669>.
- [30] B. Jasiok, E.B. Postnikov, M. Chorążewski, The prediction of high-pressure volumetric properties of compressed liquids using the two states model, *Physical Chemistry Chemical Physics* 21 (29) (2019) 15966–15973, <https://doi.org/10.1039/C9CP02448D>.
- [31] S.R. Brinkley Jr, J.G. Kirkwood, Theory of the propagation of shock waves, *Phys. Rev.* 71 (1947) 606–611, <https://doi.org/10.1103/PhysRev.71.606>.
- [32] P.L. Chueh, J.M. Prausnitz, A generalized correlation for the compressibilities of normal liquids, *AIChE J.* 15 (1969) 471–472, <https://doi.org/10.1002/aic.690150335>.
- [33] A. Grzybowski, K. Koperwas, A. Swiety-Pospiech, K. Grzybowska, M. Paluch, Activation volume in the density scaling regime: Equation of state and its test by using experimental and simulation data, *Physical Review B* 87 (2013) 054105, <https://doi.org/10.1103/PhysRevB.87.054105>.
- [34] A. Grzybowski, K. Koperwas, M. Paluch, Equation of state in the generalized density scaling regime studied from ambient to ultra-high pressure conditions, *J. Chem. Phys.* 140 (2014) 044502, <https://doi.org/10.1063/1.4861907>.
- [35] A. Grzybowski, A.R. Lowe, B. Jasiok, M. Chorążewski, Volumetric and viscosity data of selected oils analyzed in the density scaling regime, *J. Mol. Liq.* 353 (2022) 118728, <https://doi.org/10.1016/j.molliq.2022.118728>.
- [36] J. Petitet, L. Denielou, R. Tufeu, Thermodynamic properties of molten nitrates under pressure obtained from velocity of sound, *Physica B+C* 144 (1987) 320–330, [https://doi.org/10.1016/0378-4363\(87\)90013-1](https://doi.org/10.1016/0378-4363(87)90013-1).
- [37] R. Higgs, T. Litovitz, Ultrasonic Absorption and Velocity in Molten Salts, *J. Acoust. Soc. Am.* 32 (1960) 1108–1115, <https://doi.org/10.1121/1.1908357>.
- [38] L. Denielou, J.-P. Petitet, C. Tequi, D. Sirousse-Zia, Masse volumique et coefficient de dilatation des nitrates alcalins fondus et de leurs mélanges, *Journal de Chimie Physique* 74 (1977) 247–248, <https://doi.org/10.1051/jcp/1977740247>.
- [39] P. Cerisier, G. Finiels, Y. Doucet, La célérité des ultra-sons et son exploitation thermodynamique dans les mélanges de sels fondus-II. — Études de quelques halogénures et nitrates alcalins, *Journal de Chimie Physique* 71 (1974) 836–841, <https://doi.org/10.1051/jcp/1974710836>.
- [40] D. Sirousse-Zia, L. Denielou, J. Petitet, C. Tequi, Complément à l'étude thermodynamique de sels fondus à anion polyatomique, *J. de Physique Lett.* 38 (1977) 61–63, <https://doi.org/10.1051/jphyslet:0197700380206100>.