PAN
ARCHIVES OF ACOUSTICS
Vol. **43**, No. 3, pp. 537–541 (2018)

DOI: 10.24425/123925

An Improved Approximation for DIPPR-Based Predicting Speed of Sound in Long-Chained n-Alkanes

Eugene B. POSTNIKOV(1), Yuriy V. NEDYALKOV(1), Ilya POLISHUK(2)

(1) *Department of Theoretical Physics*
Kursk State University
Radishcheva st., 33, 305000 Kursk, Russia; e-mail: postnicov@gmail.com, ynedyalkov@gmail.com

(2) *Department of Chemical Engineering*
Biotechnology and Materials
Ariel University
40700, Ariel, Israel; e-mail: polishuk@ariel.ac.il

(*received May 29, 2017; accepted April 9, 2018*)

In this short communication, we revise a correlation for the saturated liquid isothermal compressibility based on the data available in DIPPR (Postnikov, 2016) which considers the molecular non-sphericity and addresses a problem of predicting speeds of sound in saturated long-chained alkanes. In addition, we correct a misprint appeared in the cited work and provide programming code used for the realisation of the proposed calculations.

Keywords: n-alkanes; isothermal compressibility; speed of sound.

1. Introduction

DIPPR (DIPPR 801 Database) is one of the most popular databases on thermophysical properties of substances. However, due to the lacking of pertinent experimental data, it does not include several important properties, such as the isothermal compressibility, isobaric thermal expansion coefficient, and speeds of sound of saturated liquids. In the previous study (Postnikov, 2016) it was demonstrated that tFhese properties can be estimated in a raw manner while implementing the available in the DIPPR data on vapour pressures, saturated liquid densities, and isobaric heat capacities. That approach was based on the Brelvi-O'Connel correlation for the isothermal compressibility (κ_T):

$$\frac{\mu_0}{RT\rho\kappa_T} = \exp\left[-0.42704\left(\xi\rho_r-1\right)+2.089\left(\xi\rho_r-1\right)^2 - 0.42367\left(\xi\rho_r-1\right)^3\right]-1. \tag{1}$$

In Eq. (1) $\rho_r = \rho/\rho_c$ (the reduced density), ρ_c is the critical density, ξ is an adjustment parameter determined using the internal pressure at the boiling point (Chorążewski *et al.*, 2015); μ_0, R, T are the molar mass, the gas constant, and the temperature, respectively. A major shortcoming of this correlation is a non-monotonic character of the cubic polynomial in respect of the reduced density. In particular, this equation exhibits a drastic decay for large reduced densities $\rho_r > 4.18$. Such reduced densities are typical for the long-chained hydrocarbons, whose saturated liquid sound velocities have not been predicted in an accurate manner (Postnikov, 2016). Moreover, $\xi \neq 1$ leads to the unphysical negative isothermal compressibility in the critical point because Eq. (1) does not reproduce accurately the transition to power law character of the isothermal compressibility in the sub-critical region.

This study aims at correcting these issues. Here we propose a more physically reasonable correlation for the isothermal compressibility resulting in more accurate predictions of speeds of sound for a larger variety of compounds.

2. The improved correlation for the isothermal compressibility

Instead of improving the dimensionless combination (1), we directly consider the isothermal compressibility. As it is known (Landau, Lifshitz, 2013), κ_T diverges as a power law function $\kappa_T \sim t^{-\gamma}$ of the order parameter $t = 1 - T/T_c$ while approaching the critical temperature T_c. Here γ is the corresponding critical index. At the same time, the density deviation from the critical value satisfies the following condition: $\rho - \rho_c \sim t^D$. D is another critical index interconnected with γ as $\gamma = 2(1-D)$: the scale invariance property (Widom, 1962). Remarkable, the DIPPR's expression for densities

$$\rho = \frac{A}{B^{1+\left(1-\frac{T}{C}\right)^D}} \tag{2}$$

satisfies the same functional form in the subcritical region. Indeed, Eq. (2) can be represented as $\rho = \rho_c \exp\left(-t^D \log B\right)$ because $C = T_c$, $A/B = \rho_c$. Consequently, using the expansion $\exp(x) \approx 1 + x$ for $t \ll 1$, we get $\rho - \rho_c = \rho_c \log B^{-1} \cdot t^D$. The latter means that the DIPPR's density coefficient D is in fact the Widom's density critical index, while the corresponding isothermal compressibility index is equal to $\gamma = 2\,(1-D)$. Since the power law is valid within the subcritical region only, we can obtain the isothermal compressibility as a function of the deviation of the reduced temperature from unity $\kappa_T = \kappa_0 g(t) t^{-\gamma}$, where $g(t) \to 1$ at $t \to 0$, and $\kappa_0 = \text{const}$.

Within a general framework of the crossovers from long range to short range correlations, we have investigated the correcting function $g(t) = \exp(\gamma_1 t)$. We have used the standard thermodynamic expression for the isothermal compressibility

$$\kappa_T = \frac{1}{\rho}\left(\frac{1}{u^2} + \frac{T\alpha_P^2}{C_P}\right)$$

with the substituted warrant speed of sound data u (Neruchev *et al.*, 2005) and DIPPR correlations (DIPPR 801 Database) for other thermodynamic parameters (the density ρ and its isobaric coefficient of expansion α_P and the isobaric heat capacity C_P) for short-chained n-alkanes from n-pentane to n-dodecane and evaluated two-stage fitting, which included minimisation of the deviation between experimental and calculated data with the subsequent polynomial interpolation of the obtained individual values of γ_1. This fitting evaluated using the build-in statistical function of SigmaPlot software has yielded the following function (the correlation coefficient 99.98%, see Fig. 1 as illustration):

$$\gamma_1 = -0.663 r_g + 0.0859 r_g^2 - 0.00432 r_g^3, \tag{3}$$

where r_g is the molecule gyration radius given in DIPPR database multiplied by the factor 10^{10}. This selection of the control parameter has been motivated by the physical assumption that the non-spherical molecular shapes should influence the packing properties, and, correspondingly, the isothermal compressibility.

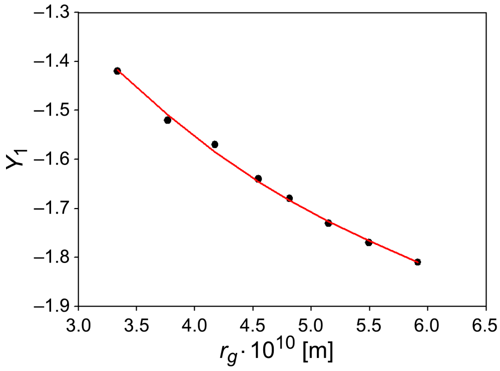

Fig. 1. Coefficients in the exponential correcting factor for the isothermal compressibility for short-chained n-alkanes from n-pentane to n-dodecane as a function of the gyration radii and their fitting by Eq. (3).

The constant κ_0 can be determined expressing the isothermal compressibility $\kappa_T^b = \kappa_0 g(t_b) t_b^{-\gamma}$ included in the respective inverse density fluctuations parameter $\nu_b = \mu_0 \left(RT_b\rho_b\kappa_T^b\right)^{-1}$ via the internal pressure at the boiling point (Postnikov, 2016)

$$P_i^b = \frac{(24.5T_b - 1400)(4.44 - 0.78\omega)\rho_b}{\mu_0}, \tag{4}$$

where ω is Pitzer's acentric factor and T_b is the boiling temperature.

Here we report that Eqs. (10) and (11) in (Postnikov, 2016) contain a misprint: there is no T_b in their denominators. However, this textual misprint did not appear in the programming code used for calculations. It is freely accessible now (Postnikov *et al.*, 2018) and all numerical and graphical results of (Postnikov, 2016) are valid. Thus, the correct form of the modified Srivastava's correlation is Eq. (4).

It should be pointed out that many long-chained hydrocarbons decompose below their boiling temperatures. Consequently, the reported by DIPPR T_b values often present raw estimations rather than experimental measurements. For this reason, we have adopted the following criterion:

$$T_b = \begin{cases} \text{if } T_b\,[\text{DIPPR}] > 0.82T_c, & T_b\,[\text{DIPPR}], \\ \text{otherwise}, & T_b = 0.82T_c. \end{cases} \tag{5}$$

This correcting replacement should be applied to n-alkanes C_nH_{2n+2} with $n \geq 23$ because the DIPPR-provided boiling temperature results in a sufficient overestimating of the speed of sound. An example of such overestimation is shown in Fig. 2, where one can see that the dash-dotted line representing the speed of sound in squalane calculated using the DIPPR-provided boiling temperature is practically parallelly shifted into the region of higher values with respect to experimental data (upward triangles) and the calculations reproducing them using the correction (5) (solid line).

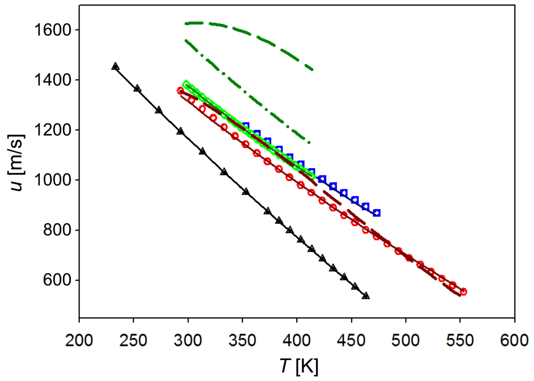

Fig. 2. Speeds of sound in saturated alkanes. Points – experimental data: circles – n-octane (Neruchev *et al.*, 2005), downward triangles – n-hexadecane (Neruchev *et al.*, 2005), crossed circles – n-tetracosane (Neruchev *et al.*, 2005), upward triangles – squalene (Korotkovskii *et al.*, 2012); solid lines – predictions of the proposed approach; dashed lines – predictions of the previous method (Postnikov, 2016) for n-hexadecane and squalene; dash-dotted line – prediction of the described approach without the boiling point correction for squalene.

In addition, the differentiated logarithm of Eq. (2) yields the following expression for the isobaric thermal expansion coefficient:

$$\alpha_P = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_P = -\frac{\mathrm{d}\log\rho}{\mathrm{d}T} = -\frac{D}{C}t^{D-1}\log B. \quad (6)$$

Therefore, utilising the thermodynamic definition of the internal pressure

$$P_i = T\frac{\alpha_P}{\kappa_T} - P \quad (7)$$

and neglecting the atmospheric pressure $P = P_a$ in the right-hand side, we obtain the following expression for the isothermal compressibility in the boiling point (i.e. $P_i = P_i^b$ here):

$$\kappa_0 = -\frac{T_b}{T_c}\frac{\mathrm{e}^{-\gamma_1\left(1-\frac{T_b}{T_c}\right)}}{P_i^b}D\left(1-\frac{T_b}{T_c}\right)^{1-D}\log B. \quad (8)$$

In addition to the DIPPR's expression for the saturated liquid densities (Eq. (2)), the proposed approach requires the data on isobaric heat capacities, which are also available in the databank. These data should be interpreted as:

$$C_p = \begin{cases} \text{if } T \le T_b, & C_s = \displaystyle\sum_{n=0}^{4} c_n T^4, \\ \text{otherwise}, & C_s - \alpha_P \dfrac{\mathrm{d}P}{\mathrm{d}T}, \end{cases} \quad (9)$$

where c_n are the DIPPR coefficients for the liquid phase isobaric heat capacity, C_s is the isobaric heat capacity of saturated liquid and

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \left(-\frac{B'}{T^2} + \frac{C'}{T} + D'E'T^{E'-1}\right) \cdot \exp\left(A' + \frac{B'}{T} + C'\log(T) + D'T^{E'}\right) \quad (10)$$

is a temperature derivative of the DIPPR's expression for the vapour pressures, whose coefficients are A', B', C', D', E', respectively.

The choice between two expressions given in Eq. (9) corresponds to the explanation to the correlations provided in (DIPPR 801 Database): for temperatures lower than the boiling point, they describe the heat capacity at the constant (normal atmospheric) pressure, i.e. C_p directly; otherwise it is the saturated heat capacity.

The isobaric expansion coefficient can be obtained as a derivative of Eq. (2) (with an additional correction for the saturation curve for temperatures larger than the boiling one):

$$\alpha_p = \begin{cases} \text{if } T \le T_b, & -\dfrac{D}{C}\left(1-\dfrac{T}{C}\right)^{1-D}\log B, \\ \text{otherwise}, & -\dfrac{D}{C}\left(1-\dfrac{T}{C}\right)^{1-D}\log B + \kappa_T\dfrac{\mathrm{d}P}{\mathrm{d}T}. \end{cases} \quad (11)$$

The isothermal compressibility should be determined as follows:

$$\kappa_T = \exp\left(a + \frac{b}{T} + c\log(T) + dT^e\right) \quad (12)$$

and $a = \log(\kappa_0)$, $b = 0$, $c = -\gamma$, $d = \gamma_1$, $e = 1$.

Note that Eq. (12) has the form called DIPPR-equation 101 and mathematically equivalent to the form $\kappa_T = \kappa_0\exp(\gamma_1 t)t^{-\gamma}$ discussed above.

All these quantities can be combined for the final calculation of the speed of sound via the standard thermodynamic formula

$$u = \left(\kappa_T\rho - \frac{T\alpha_P^2}{C_P}\right)^{-1/2}, \quad (13)$$

which can be practically used step-by-step as follows:

(i) take coefficients for a chosen liquid from DIPPR 801 database and compute for each temperature the density, the isobaric heat capacity, and the isobaric coefficients of expansion using DIPPR correlation formulae and their derivatives (2), (9)–(11);

(ii) compute the amplitude factor using Eqs. (4) and (8) as well as the exponential coefficients $\gamma = 2(1-D)$, γ_1 given by Eq. (3) using the parameters from the same source (DIPPR 801 Database);

(iii) substitute the obtained numerical parameters into Eq. (12) obtaining the isothermal compressibility;

(iv) substitute all these calculated functions into Eq. (13) that gives the desired value for the speed of sound.

To automate this procedure, we provide a free programming library (Postnikov *et al.*, 2018) for MATLAB/OCTAVE, which evaluates these calculations and exports the obtained speed of sound values into a text file. DIPPR parameters may be entered using an Excel spreadsheet. An example for n-hexane filled with the data freely available due to courtesy of DIPPR AICHE demo database (dippr.aiche.org) is provided for guidance of formatting.

3. Results

Let us evaluate the predictions yielded by the proposed approach for the speeds of sound of saturated liquid hydrocarbons. The experimental data have been reported by several sources: Neruchev *et al.*, 2005 for n-alkanes from n-octane to n-tetracosane (with exception of n-tetradecane). The latter substance was investigated by Khasanshin *et al.* (2001). The data on n-pentadecane and n-heptadecane were published by Daridon *et al.* (2002), n-octadecane – by Dutour *et al.* (2000), n-triacontane (squalane) – by Korotkovskii *et al.* (2012).

The coefficients used in Eqs. (2), (6), (10) are taken from (DIPPR 801 Database). In addition, the DIPPR density coefficient D directly gives the isothermal compressibility critical index as $\gamma = 2\,(1 - D)$.

Table 1 presents the average absolute deviations (AAD) of speed of sound predictions for alkanes. As it can be seen, these deviations do not exceed the experimental uncertainties, regardless of the chain length. The latter confirms our assumption made in Eq. (3) that the gyration radius representing the molecular non-sphericity is in fact a control parameter for the isothermal compressibility of chained hydrocarbons due to its influence on their packing properties in the liquids bulk. Moreover, the proposed approach also removes the flaws in the Brelvi-O'Connell correlation characteristic for large reduced densities (Postnikov, 2016).

Table 1. The average absolute deviations for alkanes and the corresponding temperature intervals based on the available data and the validity intervals of DIPPR correlation for isobaric heat capacity.

Liquid	Temperature interval [K]	AAD [%]
C_8H_{18}	233.15–433.15	0.65
C_9H_{20}	233.15–333.15	0.81
$C_{10}H_{22}$	293.15–463.15	0.42
$C_{11}H_{24}$	293.15–433.15	0.51
$C_{12}H_{26}$	293.15–433.15	0.24
$C_{13}H_{28}$	303.15–453.15	0.25
$C_{14}H_{30}$	303.15–433.15	0.99
$C_{15}H_{32}$	293.15–383.15	1.03
$C_{16}H_{34}$	293.15–553.15	0.52
$C_{17}H_{36}$	303.15–383.15	1.10
$C_{18}H_{38}$	313.15–383.15	1.03
$C_{19}H_{40}$	313.15–473.15	0.82
$C_{20}H_{42}$	323.15–473.15	0.24
$C_{21}H_{44}$	333.15–473.15	0.23
$C_{22}H_{46}$	333.15–473.15	0.15
$C_{23}H_{48}$	333.15–473.15	0.11
$C_{24}H_{50}$	353.15–473.15	0.48
$C_{30}H_{62}$	298.15–413.15	0.30

Figure 2 demonstrates that the accuracy of the proposed approach is independent from the reduced densities. We have chosen the same liquids which illustrated the fail of the reduced density approach in (Postnikov, 2016) and added two of them, n-hexadecane, and squalene to provide a comparative picture of the old and new approaches. One can see that the correction proposed in this work accurately predicts the decrease of the saturated speed of sound slopes with the increasing chain lengths. The main feature resulting in such an improvement is connected with the rejection of the reduced density, which was considered earlier as a main parameter and acted incorrectly for heavy molecules (see Fig. 2 for the example of squalene which demonstrates a drastic error, and n-hexadecane for which this error is smaller but exists anyway) in favour of a direct correlation of the isothermal compressibility as a function of temperature based on some scaling arguments of statistical physics. The latter appropriately fixes the basic governing property.

4. Conclusion

In the previous study (Postnikov, 2016) it was shown that saturated liquid phase properties included in the DIPPR database provide a sufficient basis for predicting the pertinent speed of sound while using the Brelvi-O'Connel correlation for the reduced isothermal compressibility. Although this approach can be implemented for different classes of organic liquids, it is restricted by the upper range of densities $\rho < 3.5\rho_c$, where ρ_c is the critical density. As a result, it could not be applied for the industrially important substances such as heavy alkanes.

In this work, we have developed a correction solving this problem and expanding the applicability range of the model. The proposed approach directly operates with the isothermal compressibility, fulfills the exact scale invariance conditions in the subcritical region, and admits expectable functional dependence of transitions between critical and non-ctitical states. For the latter ones, we have proposed a numerical correlation based on the gyration radius, which is a natural measure for the molecular non-sphericity. In addition, we have revealed the interplay between Widom's density critical index and one of the DIPPR reference constants. The proposed approach can be successfully implemented for a wide range of saturated state parameters, which can be particularly important for various practical purposes.

Acknowledgment

EBP and YVN are supported by RFBR, research project No. 16-08-01203.

References

1. Chorążewski M., Postnikov E.B., Oster K., Polishuk I. (2015), *Thermodynamic properties of 1,2-dichloroethane and 1, 2-dibromoethane under elevated pressures: experimental results and predictions of a novel DIPPR-based version of FT-EoS, PC-SAFT, and CP-PC-SAFT*, Industrial & Engineering Chemistry Research, **54**, 39, 9645–9656.
2. Daridon J.L., Carrier H., Lagourette B. (2002), *Pressure dependence of the thermophysical properties of n-pentadecane and n-heptadecane*, International Journal of Thermophysics, **23**, 3, 697–708.
3. Dutour S., Daridon J.L., Lagourette B. (2000), *Pressure and temperature dependence of the speed of sound and related properties in normal octadecane and nonadecane*, International Journal of Thermophysics, **21**, 1, 173–184.
4. DIPPR 801 Database, http://www.aiche.org/dippr/events-products/801-database, retrieved on 09.06.2018.
5. Khasanshin T.S., Shchemelev A.P. (2001), *Sound velocity in liquid n-alkanes*, High Temperature, **39**, 1, 60–67.
6. Korotkovskii V.I., Lebedev A.V., Ryshkova O.S., Bolotnikov M.F., Shevchenko Y.E., Neruchev Y.A. (2012), *Thermophysical properties of liquid squalane $C_{30}H_{62}$ within the temperature range of 298.15–413.15 K at atmospheric pressure*, High Temperature, **50**, 4, 471–474.
7. Landau L.D., Lifshitz E.M. (2013), *Statistical Physics. Part 1*, Elsevier.
8. Neruchev Y.A., Bolotnikov M.F., Zotov V.V. (2005), *Investigation of ultrasonic velocity in organic liquids on the saturation curve*, High temperature, **43**, 2, 266–309.
9. Postnikov E.B. (2016), *Can DIPPR database be used for an estimation of the speed of sound? A case study of liquid hydrocarbons*, Archives of Acoustics, **41**, 4, 713–719.
10. Postnikov E.B., Nedyalkov Y.V., Polishuk I. (2018), *DIPPR-based prediction of the speed of sound*, Mendeley Data, http://dx.doi.org/10.17632/ zshnj5c7v7.1
11. Widom B. (1962), *Relation between the compressibility and the coexistence curve near the critical point*, Journal of Chemical Physics, **37**, 11, 2703–2704.