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Simultaneous free-volume modeling of the self-diffusion coefficient and dynamic viscosity at high pressure

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In this work, a simultaneous modeling of the self-diffusion coefficient and the dynamic viscosity is presented. In the microstructural theory these two quantities are governed by the same friction coefficient related to the mobility of the molecule. A recent free-volume model, already successfully applied to dynamic viscosity, has been considered and generalized. In this generalized model the compound is characterized by only four parameters. But if the quadratic length is known, the number of adjustable parameters is three. The compounds considered in this work are benzene, carbon tetrachloride, chlorotrifluoromethane, cyclohexane, methylcyclohexane, and tetramethylsilane. For these pure compounds we have found in the literature several data for both the self-diffusion and the dynamic viscosity in large viscosity, diffusion, temperature, and pressure intervals (up to around 500 MPa for methylcyclohexane and tetramethylsilane). The average absolute deviation obtained by the modeling is generally less than 3% for the viscosity and 5% for the self-diffusion.

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INTRODUCTION

Very recently [1] in a work on molecular dynamic it has been stressed that the pressure (P) dependence of transport properties (in particular the dynamic viscosity η and the self-diffusion coefficient D) has drawn much less attention compared to their temperature (T) dependence. Many questions regarding pressure dependence are still either not known or poorly understood. In particular the authors [1] wondered what is the correlation between the pressure and temperature dependence of viscosity and diffusion and they said that they were not aware if these questions have already been satisfactorily answered. In their paper the authors carried out extensive molecular dynamic simulations with the Kob-Andersen model of binary mixtures emphasizing the role of the free volume. In the same opinion a connection between the generic van der Waals equation of state and the self-diffusion coefficient of liquids has recently been proposed [2] with the free volume computed from the cavity function obtained by means of a Monte Carlo cavitation method and some comparisons have been made on spherical molecules (argon and methane in approximation). The dynamic viscosity was not considered in this work. Nevertheless, Liu *et al.* [3] have proposed a generalized free-volume theory for transport properties and new trends about the relationship between the free volume and equations of state, considering both dynamic viscosity and self-diffusion coefficient.

In this work we intend to use the link that appears between dynamic viscosity and self-diffusion coefficient in microscopic theory. It has theoretically been demonstrated (see

for instance Refs. [4,5]) that the viscosity in the dense state may be written as

$$\Delta \eta = \frac{\rho N_a \zeta L^2}{M}, \quad (1)$$

where N_a is Avogadro's number, ζ the friction coefficient of a molecule, L the average characteristic molecular quadratic length, ρ the density of the compound and M the molecular weight. The friction coefficient ζ is related to the mobility of the molecule. The self-diffusion coefficient has often been theoretically developed (see, for instance, Refs. [6–9]) and particularly for small molecules by Doi and Edwards [6] in the case of the Rouse theory, obtaining the following expression:

$$D = \frac{kT}{\zeta}. \quad (2)$$

The combination of Eqs. (1) and (2) leads to $DM\Delta\eta/\rho RT = L^2$ (where $R = kN_a$ is the ideal gas constant). This equation is similar to $DM\Delta\eta/\rho RT = \delta^2/2$ which corresponds to the so-called Dullien's invariant [8,10] first derived by using Lamm's theory in order to evaluate a molar average friction coefficient. In this equation the parameter δ is the average momentum transfer distance. The Dullien's invariant is not based on any particular model of the liquid state and is expected to hold for Newtonian liquids. Dullien showed that his equation is consistent with elementary kinetic theory.

Equations (1) and (2) show that an important issue is the evaluation of the molecular friction coefficient ζ . In the following we will present and use a possibility related to the expression of ζ proposed in a recent free-volume model for the dynamic viscosity [5,11]. This model has been introduced in order to model the viscosity of Newtonian fluids in

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TABLE I. Deviations obtained with the free-volume model, using four parameters.

	C ₆ H ₆	CClF ₃	C ₆ H ₁₂	C ₇ H ₁₄	C ₇ H ₁₄ ($P \leq 200$ MPa)	CCl ₄	C ₄ H ₁₂ Si	C ₄ H ₁₂ Si ($P \leq 210$ MPa)
L (Å)	2.177	1.76447	2.38095	2.66377	2.63858	2.082716	2.086599	2.1263
b_f (Å)	8.43783	7.39201	8.45667	10.9092	10.04008	5.88255	6.665568	6.23138
α (J m ³ /mol/kg)	73.9411	23.5357	75.2126	100.2599	90.59632	38.10547	92.78703	81.1812
B	0.011458	0.015659	0.017541	0.009414	0.010825	0.012222	0.007363	0.008731
$D_{av,D}$ (%)	2.14	3.09	1.56	8.50	5.06	3.08	5.85	4.05
$D_{max,D}$ (%)	8.68	11.31	5.75	27.34	14.69	8.2	17.88	10.88
B_D (%)	0.17	-0.37	-0.025	2.29	-0.52	0.68	2.46	1.91
$D_{av,\eta}$ (%)	0.84	3.85	1.74	6.35	2.23	1.084	2.33	2.64
$D_{max,\eta}$ (%)	7.97	8.29	5.95	22.76	6.69	4.50	8.58	11.36
B_η (%)	-0.18	0.097	-0.30	-1.82	-0.26	-0.15	-0.83	1.21

both gaseous and dense states. It has been successfully applied to various hydrocarbons [5] over wide ranges of temperature and pressure. For instance this model can represent the data of methane (database of 885 points) from 0.01 MPa to 200 MPa and from 90.7 K to 600 K (i.e., from dilute gas to dense state) with an average absolute deviation of 2.59% and a maximum deviation of 14.8% at $P=200$ MPa. The model has also been applied at high pressure, i.e., above 250 MPa and sometimes up to 500 MPa, to benzene (0.72% and 6.56%), trans-decalin (2.03% and 8.34%), *n*-hexane (1.09% and 6.50%), *n*-dodecane (3.51% and 18.5%) and *n*-octane (2.51% and 19.6%) data. The pressure, temperature and viscosity intervals are sufficiently large to verify that the viscosity free-volume model is not a local fit of the data.

PRESENTATION OF THE MODEL

In the free-volume approach used in this work, the total dynamic viscosity is given by $\eta = \eta_0 + \Delta\eta$. The first term is a dilute gas contribution and the second one $\Delta\eta$ is the dense state contribution. The dilute gas viscosity η_0 is defined as the viscosity at the dilute gas limit and, for several fluids can be accurately represented by the Chung *et al.* model [12]. The applied approach connects the term $\Delta\eta$ to molecular structure via a representation of the free volume fraction. The viscosity, in this theory, appears as being the product of the fluid modulus $\rho RT/M$ by the mean relaxation time of the molecule defined by $L^2\zeta/(kT)$. The friction coefficient ζ is related to the mobility of the molecule and to the diffusion process Eq. (2). Notice here that in the case of the theoretical explanation of the movement of a colloidal particle at infinite dilution Eq. (2) is the Einstein equation. The use of the expression of the friction coefficient for a macroscopic sphere gives the Stokes-Einstein relation. But here, the friction coefficient has to be the one associated with a molecule and we use a free volume framework as developed in Ref. [5]. As Doolittle [13] has shown, this coefficient is governed by the free volume fraction $f_v = v_f/v$ where v is the specific molecular volume; v_0 the molecular volume of reference or hard-core volume, and $v_f = (v - v_0)$. At temperature T it has been shown [5] that $f_v = (RT/E)^{3/2}$. To establish this relation

it is assumed that the molecule moves in a potential field controlled by the intermolecular energy E due to the neighboring molecules. This intermolecular energy can be approximated [5] by $E = \alpha\rho + PM/\rho$ where the term $PM/\rho = PV$ is connected to the energy necessary to form the vacant vacuums available for the diffusion of the molecules. $E_0 = \alpha\rho$ is connected to the energy barrier that the molecule has to exceed in order to diffuse. With these hypotheses and using the Doolittle result [13], which has later been theoretically justified by Cohen and Turnbull [14], Allal *et al.* [5] have shown that the viscosity of the dense state is given by

$$\Delta\eta = \frac{\rho N_a L^2 \zeta_0 \exp(B/f_v)}{M},$$

where B characterizes the free volume overlap, and

$$\zeta_0 = \frac{E}{N_a b_f} \sqrt{\frac{M}{3RT}},$$

where b_f is the dissipation length of the energy E . Finally,

$$\eta = \eta_0 + \frac{\rho L^2 \left(\alpha\rho + \frac{PM}{\rho} \right)}{b_f \sqrt{3RTM}} \exp \left(B \left(\frac{\alpha\rho + \frac{PM}{\rho}}{RT} \right)^{3/2} \right). \quad (3)$$

This equation involves four physical parameters characterizing the molecule: L , b_f , α , and B . However, as it is shown below, L can be evaluated independently and the number of parameters reduces to three. Combining Eqs. (1) to (3) it follows for the self-diffusion coefficient:

$$D = \frac{RTb_f}{PM} \sqrt{\frac{3RT}{M}} \exp \left(-B \left(\frac{\alpha\rho + \frac{PM}{\rho}}{RT} \right)^{3/2} \right), \quad (4)$$

which involves the same parameters as for the dynamic viscosity: b_f , α and B . In the following section, Eqs. (3) and (4) are regressed to experimental D and η data for several compounds over wide temperature and pressure intervals, corre-

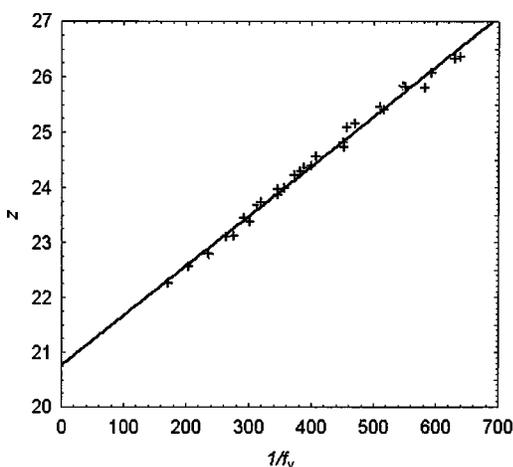


FIG. 1. Variations of z versus $1/f_v$ in the case of methylcyclohexane (+: experimental data; —: best straight line). [For the calculation of z all the units are in SI and the value for $1/f_v=0$ allows us to evaluate $\ln(b_f)$ with b_f expressed in meters.]

sponding to large viscosity and self-diffusion intervals, in order to show the coherence of this description.

DATABASE AND CHARACTERIZATION OF THE RESULTS

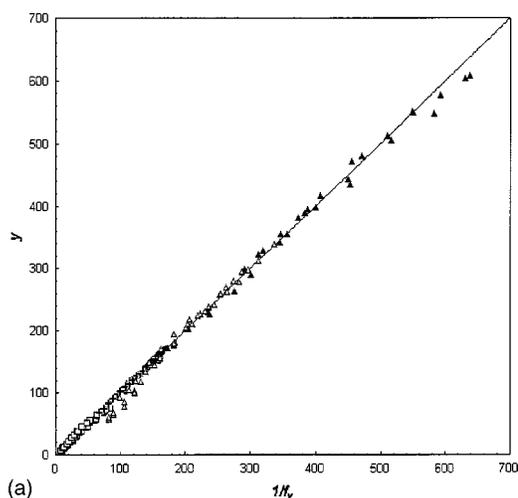
The main purpose of this paper is to show that the high-pressure dynamic viscosity and self-diffusion coefficient behavior can be modeled using strictly the same molecular parameters. Additionally, the average characteristic molecular quadratic length L values evaluated from those models are compared with the values obtained with an independent method.

The following substances have been considered in this work.

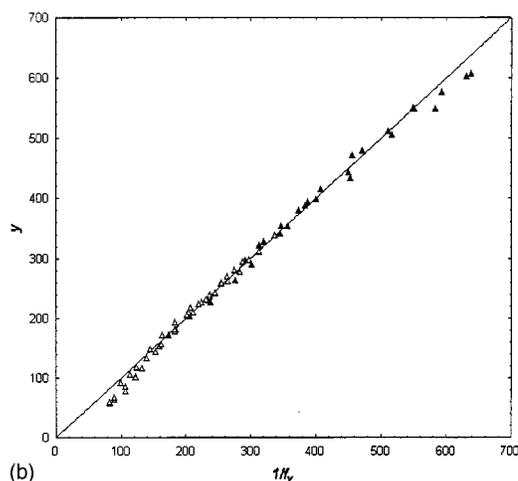
Benzene [15,16]: C_6H_6 , $M=78.113$ g/mol, 39 values for η (estimated 2% uncertainty) and 39 values for D (2% up to 4% uncertainty), between $288.2\text{ K} \leq T \leq 333.2\text{ K}$ and $0.101\text{ MPa} \leq P \leq 154.4\text{ MPa}$. Viscosity range $0.390 < \eta < 1.157\text{ mPa}\cdot\text{s}$. Self-diffusion range $1.36 < D < 3.699 \cdot 10^{-9}\text{ m}^2\text{ s}^{-1}$.

Chlorotrifluoromethane [17]: $CClF_3$, $M=104.459$ g/mol, 26 values for η (uncertainty not indicated) between $303.15\text{ K} \leq T \leq 348.15\text{ K}$ and $5\text{ MPa} \leq P \leq 60\text{ MPa}$ and 67 values for D (2% uncertainty), between $303.15\text{ K} \leq T \leq 348.15\text{ K}$ and $3.68\text{ MPa} \leq P \leq 188.38\text{ MPa}$. However the curve $\eta(P)$ at 303.15 K seems to show that the viscosity value at 5 MPa is not correct (perhaps a typographical mistake). So this point has not been included in the calculation. Viscosity range $0.019 < \eta < 0.189\text{ mPa}\cdot\text{s}$. Self-diffusion range $3.20 < D < 60.2 \cdot 10^{-9}\text{ m}^2\text{ s}^{-1}$.

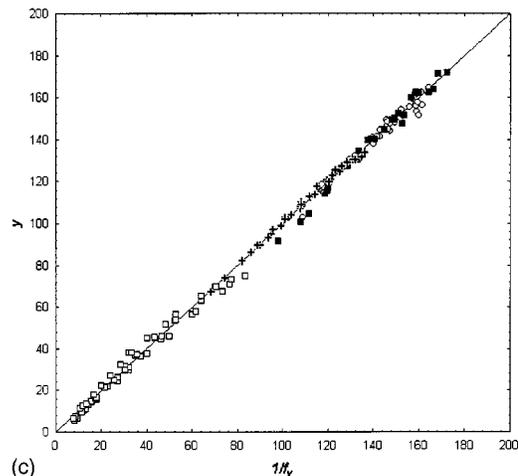
Cyclohexane [18]: C_6H_{12} , $M=84.161$ g/mol, 25 values for η (uncertainty not indicated) between $313\text{ K} \leq T \leq 383\text{ K}$ and $0.1\text{ MPa} \leq P \leq 210\text{ MPa}$ and 39 values for D (uncertainty not indicated), between $313\text{ K} \leq T \leq 383\text{ K}$ and $0.1\text{ MPa} \leq P \leq 214\text{ MPa}$. Viscosity range $0.319 < \eta < 1.72\text{ mPa}\cdot\text{s}$. Self-diffusion range $1.03 < D < 5.237 \cdot 10^{-9}\text{ m}^2\text{ s}^{-1}$.



(a)



(b)



(c)

FIG. 2. Master curve y versus $1/f_v$. (a) All the data. \circ : benzene; \blacksquare : CCl_4 ; \square : chlorotrifluoromethane; $+$: cyclohexane; \blacktriangle : methylcyclohexane; \triangle : tetramethylsilane; —: first bisectrix. (b) \blacktriangle : methylcyclohexane; \triangle : tetramethylsilane; —: first bisectrix. (c) \circ : benzene; \blacksquare : CCl_4 ; \square : chlorotrifluoromethane; $+$: cyclohexane; —: first bisectrix.

Methylcyclohexane [19]: C_7H_{14} , $M=98.188$ g/mol, 22 values for η (uncertainty not indicated) between $223\text{ K} \leq T \leq 298\text{ K}$ and $0.1\text{ MPa} \leq P \leq 500\text{ MPa}$ and 30 values for D (5% uncertainty up to 15% at higher pressures), between

TABLE II. Comparison between the L values (in Å) obtained in this work and calculated with a group contribution method [28].

	C ₆ H ₆	CClF ₃	C ₆ H ₁₂	C ₇ H ₁₄	C ₇ H ₁₄ ($P \leq 200$ MPa)	CCl ₄	C ₄ H ₁₂ Si	C ₄ H ₁₂ Si ($P \leq 210$ MPa)
L (free volume)	2.177	1.76447	2.38095	2.66377	2.63858	2.082716	2.086599	2.1263
L (calculated)	2.1069	1.8349	2.2306	2.3629	2.3629	2.1257	2.3316	2.3316

203 K $\leq T \leq 298$ K and 0.1 MPa $\leq P \leq 500$ MPa. The data point $P = 150$ MPa and $T = 203$ K is obviously erroneous and has not been considered. Viscosity range $0.683 < \eta < 71.38$ mPa s. Self-diffusion range $0.012 < D < 1.915 \cdot 10^{-9}$ m² s⁻¹.

Tetrachloride carbon [20]: CCl₄, $M = 153.823$ g/mol, 27 values for η (estimated 2% uncertainty) and 27 values for D (2% up to 4% uncertainty), between 283.2 K $\leq T \leq 328.2$ K and 0.101 MPa $\leq P \leq 147.5$ MPa. Viscosity range $0.62 < \eta < 2.28$ mPa s. Self-diffusion range $0.51 < D < 2.08 \cdot 10^{-9}$ m² s⁻¹.

Tetramethylsilane [21,22]: C₄H₁₂Si, $M = 88.22$ g/mol, 45 values for η (uncertainty not indicated) between 298 K $\leq T \leq 373$ K and 4.6 MPa $\leq P \leq 450$ MPa and 42 values for D (uncertainty not indicated), between 298 K $\leq T \leq 373$ K and 4.5 MPa $\leq P \leq 450$ MPa. Viscosity range $0.173 < \eta < 3.805$ mPa s. Self-diffusion range $0.329 < D < 7.466 \cdot 10^{-9}$ m² s⁻¹.

These substances are in the dense state, and the pressures up to 500 and 450 MPa for methylcyclohexane and tetramethylsilane respectively, allowing to verify the performance of the model up to high pressure. In fact not only the pressure interval but also the temperature, viscosity and self-diffusion intervals are sufficiently large to check that the presented expressions are not a local fit of the data. For these six compounds the total number of data is 185 for the dynamic viscosity and 245 for the self-diffusion coefficient. All of the scaling parameters required in the Chung *et al.* dilute gas viscosity model [12] have been taken from Reid *et al.* [23]. However, in the case of tetramethylsilane, the critical constants were taken from the compendium by Simmrock *et al.* [24], and the acentric factor was estimated after an optimization of the normal boiling temperature with the Peng-Robinson equation of state [25]. We estimated for this compound: $T_c = 448.6$ K, $P_c = 2.82$ MPa, $V_c = 361$ cm³/mol and $\omega = 0.2426$. Concerning the evaluation of η_0 it is important to stress that in the dense state the dilute gas viscosity is negligible in comparison to the total viscosity.

In order to validate and compare the performance of the considered models it is necessary to introduce characteristic quantities of the results obtained. For instance, for dynamic viscosity, the following quantities are defined:

$$d_{i,\eta} = (1 - \eta_{\text{calc},i} / \eta_{\text{expt},i}) 100\%,$$

$$\mathcal{D}_{\text{av},\eta} = \frac{1}{N_b} \sum_{i=1}^{N_b} |d_{i,\eta}|,$$

$$\mathcal{B}_\eta = \frac{1}{N_b} \sum_{i=1}^{N_b} d_{i,\eta},$$

$$\mathcal{D}_{\text{max},\eta} = \max |d_{i,\eta}|,$$

in which N_b is the number of experimental points, η_{expt} the measured viscosity and η_{calc} the calculated value. The equivalent quantities are defined for self-diffusion coefficient substituting “ D ” in place of “ η .” The quantity \mathcal{D}_{av} (average absolute deviation) indicates how close the calculated values are to the experimental values and the quantity \mathcal{B} indicates how well the experimental points are distributed around the calculated curves. If $\mathcal{B} = \mathcal{D}_{\text{av}}$ then all of the experimental points are above the calculated curves. Finally, \mathcal{D}_{max} characterizes the maximum absolute deviation that is obtained using a given representation.

RESULTS OF THE NUMERICAL ANALYSIS

Table I displays the results obtained with this model, fitting simultaneously the four parameters L , b_f , α and B . In the case of methylcyclohexane and tetramethylsilane the results have been obtained first considering only data up to around 200 MPa and then all the data up to around 500 MPa. Clearly, when the pressure is limited to $P \leq 200$ MPa an important improvement is appreciated: $\mathcal{D}_{\text{max},D}$ falls from 27.3% to 14.7% and $\mathcal{D}_{\text{max},\eta}$ from 22.8% to 6.7%. This may in part be due to the larger uncertainty for the high pressure measurements and we could consider that a good agreement between experimental and calculated values for viscosity and diffusion coefficient as shown in Table I, even at pressure up to 500 MPa. Not only the pressure interval (0.1 < P < 500 MPa), but also the temperature (203 < T < 373 K), viscosity (0.019 < η < 71.38 mPa s) and self-diffusion coefficient (0.012 < D < 60.2 $\cdot 10^{-9}$ m² s⁻¹) intervals are sufficiently large to conclude that the presented expressions are not a local fit of the data.

Using the experimental values D_{expt} of the diffusion coefficient the quantity $z = -\ln(D_{\text{expt}} E / RT \sqrt{M/3RT})$ is calculated. In order to evaluate E the estimated value of α given in Table I is used, as $E = \alpha \rho + PM/\rho$. Following Eq. (4) one has $z = -\ln(b_f) + B(E/RT)^{3/2}$ and the curve z versus $(E/RT)^{3/2} = 1/f_v$ should be a straight line. The slope allows to evaluate B and the value for $1/f_v = 0$ allows to evaluate $\ln(b_f)$, i.e., b_f . Figure 1 corresponds to the worst case of Table I, i.e., for methylcyclohexane up to 500 MPa. (For this figure b_f is expressed in meters because for the calculation of z all the units are in SI.) The numerical analysis of the straight line gives $B = 0.00903$ (0.009414 in Table I) and b_f

TABLE III. Deviations obtained with the free-volume model, using three parameters and the L values calculated with a group contribution method [28].

	C ₆ H ₆	CClF ₃	C ₆ H ₁₂	C ₇ H ₁₄	C ₇ H ₁₄ ($P \leq 200$ MPa)	CCl ₄	C ₄ H ₁₂ Si	C ₄ H ₁₂ Si ($P \leq 210$ MPa)
b_f (Å)	9.97741	7.35437	8.4543	8.752098	7.732193	6.24395	6.298183	6.110199
α (J m ³ /mol/kg)	75.68944	23.6037	75.8980	100.1666	92.95238	37.8817	79.6128	74.99682
B	0.01234	0.015080	0.017587	0.009038	0.009878	0.01256	0.008000	0.009120
$D_{av,D}$ (%)	4.1	3.28	3.63	9.96	11	3.68	16.28	8.91
$D_{max,D}$ (%)	13.4	12.3	9.39	27.03	21.6	8.58	30.55	20.08
B_D (%)	4.04	-1.26	3.58	8.52	9.52	-2.48	-16.2	-8.78
$D_{av,\eta}$ (%)	2.42	5.75	8.58	13.05	8.74	1.66	5.78	7.18
$D_{max,\eta}$ (%)	6.35	14.09	14.78	23.5	18.67	6.42	16.67	14.11
B_η (%)	2.36	-5.30	8.58	13.05	8.74	-1.1	-5.61	-6.87

$=9.6226$ Å (10.9092 Å in Table I), but in that case the evaluations of B and b_f are independent of the viscosity, contrary to the values indicated in Table I, which take into account the viscosity behavior. In order to build a master curve, we have considered the dimensionless quantity $y = -(1/B)\ln(D_{\text{expt}}/E/RTb_f\sqrt{M/3RT})$ which, according to Eq. (4), is equal to $(E/RT)^{3/2} = 1/f_v$, and the curve y versus $1/f_v$ should be the first bisectrix. We used the α , B and b_f values given in Table I, because they also take into account the viscosity behavior of the compounds. All the 245 diffusion coefficient data points are plotted on Fig. 2(a). The agreement is very good (the best line corresponds to $y = -0.318 + 0.9935/f_v$). This validates in some sense the 3/2 power in the expression of f_v versus E/RT . Concerning the 3/2 power, the interested reader will find other theoretical considerations for free volume in Refs. [26], [27]. In order to clarify the figure, we plotted on Fig. 2(b) only tetramethylsilane and methylcyclohexane (up to 500 MPa) and on Fig. 2(c) we plotted benzene, chlorotrifluoromethane, cyclohexane, and tetrachloride carbon.

Another interesting point is that it is possible to evaluate the average characteristic molecular quadratic length L^2 by an independent method [28]. Assuming that the molecules are quasispherical (which is a reasonable hypothesis for the considered molecules), $L^2 = 3/5r^2$ where r is the molecular radius and L , the square root of the average characteristic molecular quadratic length, is the gyration radius. The molecular radius r is estimated from the Van der Waals volume (V_w) of the molecule calculated using a group contribution method [28] and $V_w = 4/3\pi r^3$. Table II shows a good agreement with both methods in the estimation of L . The worse case corresponds to tetramethylsilane and methylcyclohexane for which the spherical molecule hypothesis is not accurate enough resulting in a departure of about 10%. The good agreement between the molecular size L calculated in this work and the values evaluated by an independent method is an important point showing the pertinence of the used equations and their validity over wide viscosity and diffusion intervals. Finally Table III presents the results obtained using the calculated values of L and fitting the remaining 3 parameters. This reduction of the number of adjustable parameters

leads to slightly higher deviations but the results remain very good.

CONCLUSIONS

The objective of this work was to simultaneously model and predict the temperature-pressure variations of the dynamic viscosity and the self-diffusion coefficient of small molecules from the knowledge of the molecular dimensions and the energy of interaction, using the free-volume concept. To our knowledge no such simultaneous modeling, with numerical checking in such large pressure, temperature, viscosity and self-diffusion intervals, exists in the literature.

The results of this work show three key points.

(1) The satisfying agreement between our model and the experimental results is due to the good modeling of the molecular friction coefficient ζ . The correct definition of this last property is made possible by the use of the well-known microscopic theory relation between dynamic viscosity and self-diffusion coefficient.

(2) The relationship between the viscosity and the self-diffusion coefficient involves the molecular dimension L . The results of this paper show a good agreement between the fitted molecular size parameter and the actual dimension of the studied molecules. This dimension can be calculated using an independent molecular mechanical approach.

(3) The last key point concerns the energy of interaction E . The relationship between the energy and the density is an interesting ersatz but in reality we have to determine it from the electronic structure of the molecules and their spatial conformations: molecular dynamic could be a good way to do it.

Finally, this model emphasizes the relation between microstructure, free volume, and different complex thermophysical properties such as dynamic viscosity and self-diffusion coefficient. Thus, this approach may also lead to a better understanding of the relationship between a larger set of properties. In a future work the relationship between free volume, dynamic viscosity, self-diffusion coefficient and other properties will be considered.

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