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Free-volume viscosity model for fluids in the dense and gaseous states

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A free-volume and friction viscosity model is presented versus pressure and temperature, valid for both gaseous and dense fluids. This model involves only three adjustable parameters for each pure compound. It is able to represent the gas-liquid transition and the behavior in the supercritical conditions. The model has been successfully applied to methane (885 data points for $0.01 \leqslant P \leqslant 200$ MPa and $90.7 \leqslant T \leqslant 600$ K) and to propane (1085 data points for $0.01 \leqslant P \leqslant 200$ MPa and $90 \leqslant T \leqslant 600$ K) in the gaseous and dense states (average absolute deviation is 2.59% for methane and 2.50% for propane, with maximum deviation of 14.8% for methane and 9.19% for propane). It has also been applied to hexane, octane, dodecane, benzene, trans-decaline, and 2,2-dimethylpropane (903 data points) in a large pressure range (up to 505.5 MPa). Considering these compounds the maximum deviation is 19.5% (for octane) and the average deviation is 3.51% in the worst case (dodecane, which has data points up to 501.6 MPa).

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INTRODUCTION

The dynamic viscosity η of fluids is of great interest in various research areas both applied and fundamental. There is a need for reliable and accurate analytical method for viscosity calculations. Moreover the theoretical understanding of the viscosity behavior is fundamental. A large number of results are dedicated to the variation of η versus temperature and chemical species, but many experimental studies are carried out only at normal pressure. The experimental studies as a function of pressure are less frequent, however their number is increasing. In order to understand the results it is necessary to develop satisfactory models. The problem of the representation of the pressure-temperature variations of viscosity is widely open and not closed and the literature contains many different viscosity models. Recently, a critical review of predictive and correlative methods for viscosity has been made by Monnery, Svrcek, and Mehrotra [1], which considers models with theoretical basis, semitheoretical basis (they have a theoretical basis or framework but some parameters are adjustable and determined from experimental data), or entirely empirical basis. Various approaches have been presented. For gases there is, for example, the kinetic theory of gases (dilute gas viscosity), modified kinetic theory in order to take into account the effects of molecular shape and anisotropic molecular forces, corresponding state relationship. For liquids, few simple and accepted theories have been developed. Most theoretical models for gases or liquids are based on statistical mechanics and may be classified as the distribution function theory or the correlation function theory. Monnery, Svrcek, and Mehrotra [1] emphasize the fact that the accuracy of the molecular dynamics approach depends on how accurately the intermolecular potential energy functions represent the molecular interactions. But if this method is promising the results are not yet very accurate. In a recent works [2,3] Dysthe, Fuchs, and Rousseau found that the viscosity is underestimated at high densities (they found up to 80% deviation for decane, 75% for hexadecane). In any case molecular dynamics simulations are not yet a practical mean for calculating viscosity. The semitheoretical models for dense gases and liquids are based on the principle of corresponding states or may be categorized as applied statistical mechanics models such as the reaction rate theory, hard sphere (Enskog) theory, square well theory, significant structure theory, or the Lennard-Jones model. We mention also some models that use a T-η-P pseudoequation of state (T is the temperature and P the pressure).

However, many of the viscosity models are only suitable for predicting accurately either the liquid or the gas phase viscosity. One of the difficulties in developing a model is to describe correctly the transition between the low-density state (where the dilute gas viscosity is very well described by theories with the collision integral) and the high-density state (methane can be an example for petroleum engineering). In the following we propose an approach in order to model the viscosity of Newtonian fluids, based on the free-volume concept and on the diffusion models of the molecules, which is able to describe accurately such a transition. Let us recall here that, just as the mass (concentration of tracer, for example) or heat, the momentum of a fluid can be transported by diffusion. Contrary to concentration and heat, momentum is vectorial. However, the diffusion equation of momentum shows that kinematic viscosity η/ρ (ρ is the density) is like a coefficient of diffusion for momentum, similar to the coefficients D for concentration or κ for heat. Our model tries to connect viscosity to molecular structure.

BACKGROUND

The very well-known model of dynamic viscosity proposed by Eyring and collaborators [4] leads to the Arrhenius

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equation type $\eta = A\exp(B/T)$. This model describes the behavior of many low-weight molecular liquids. But it is not satisfactory for many other liquids as various articles have stressed (see, for example, [5] and [6]). This is mainly due to the fact that it involves only one mechanism of molecular relaxation. A modification of the model has been proposed by Ree, Ree, and Eyring [7]. By applying the significant structure theory of liquids to transport phenomena, the equation for viscosity is derived for hard-sphere systems. The modification consists in expressing viscosity in the following form $\eta = \eta_s(v_s/v) + \eta_g(v - v_s)/v$, where v_s is the specific volume of the solid and v that of the liquid. The authors [7] consider that the liquid consists of ''quasisolid'' molecules having only degrees of freedom for vibration and ''quasigas'' molecules with degrees of freedom for translation. The term η_g is a term of ''quasigas'' viscosity derived from kinetic theory. For simple liquids the agreement between theory and experiment is satisfactory.

Cohen and Turnbull [8] have developed a transport theory based on free volume. This theory assumes that the fluid consists of hard spheres. This theory is based on the concept that statistical redistribution of the free volume occasionally opens up voids large enough for diffusive displacement. Molecular diffusion is possible when a vacant volume (larger than minimal v^*, which allows the displacement of a molecule) is present in the liquid, then a molecule can jump into the vacancy. The average free volume v_f is defined as being the difference between the volume v of the cage, which contains the molecule, and the hard volume v_0 of the molecule. The theory leads to $\ln(\eta/\sqrt{T}) = A' + (B'/v_f)$ where $v_f = v - v_0$. This theory has been applied to simple van der Waals liquids and liquid metals. As the authors have emphasized, their theory justifies the empirical relation proposed by Doolittle [9],

$$\eta = Ae^{B/f_v}, \tag{1}$$

where f_v is the free-volume fraction and where B (which is positive) is characteristic of the free-volume overlap. As it will be shown below there are at least two possibilities to define this quantity. The basic idea is that the resistance to the flow depends on the relative number of molecules compared to free volume, which is intuitively acceptable.

A substantial number of developments have been based on the above ideas. Let us state here that the idea of free volume was naturally used for polymers (see, for example, [10] and [11]), of course in the liquid state. The interested reader can refer to Ferry's work [12] on the viscoelastic properties of polymers. Besides, some theories combine the two approaches of Eyring and Cohen and Turnbull (for example, [5]). They generally lead to an evaluation of the free volume of the liquids, larger than that suggested by the theory of Cohen and Turnbull. The free-volume idea appears then in various forms (for example, [13] and [14]). Among recently published work Wang Fredenslund, and Liu [15] have developed a model based on this idea, which provides an average absolute deviation $\mathcal{D}_{\rm av}$ on viscosity of 4.1% for 1169 experimental data including 25 pure compounds (polar and nonpolar) and 3.3% for 1142 data including 10 binary mixtures. They do not provide indications on the maximum absolute deviation. The experimental conditions covered a pressure range that reaches, in some cases, 500 MPa. For pure compounds, the worst result is obtained for water (6.8%), ethanol (5.4%), and *n*-propanol (4.8%). Their theory uses four adjustable parameters for each pure compound and two additional parameters per binary, these last parameters having to be adjusted at each temperature. Moreover it is necessary to know the density. They modified the theory of liquids proposed by Macedo and Litovitz [5], and instead of describing the variation of p_v (probability that there is sufficient local free volume for a jump to occur) with an exponential expression they assume that p_v is proportional to the free volume. Moreover they consider the activation energy in Eyring's theory not as a constant but proportional to the inverse of the molar volume. But they did not give any results at low pressures (i.e., low dense fluids), probably because their relation predicts a zero viscosity while density tends towards zero, and this is not in agreement with the viscosity of the dilute gas. They obtained $\mathcal{D}_{\rm av} = 4.2\%$ for methane ($100 \leqslant T \leqslant 400\,\mathrm{K}$ and $1 \leqslant P \leqslant 50\,\mathrm{MPa}$ with 48 data points). For propane they obtained $\mathcal{D}_{\rm av} = 3.1\%$ ($297 \leqslant T \leqslant 523\,\mathrm{K}$ and $5 \leqslant P \leqslant 80\,\mathrm{MPa}$ with 36 data points). They give also results for hexane (up to 50 MPa, $\mathcal{D}_{\rm av} = 3.6\%$), octane (up to 50 MPa, $\mathcal{D}_{\rm av} = 4.2\%$), dodecane (up to 200 MPa, $\mathcal{D}_{\rm av} = 1.8\%$), and benzene (up to 50 MPa, $\mathcal{D}_{\rm av} = 3.0\%$). Let us state also that Doolittle's relation allows a good estimate of the pressure of vitreous transition of compounds such as glycerol and dibuthylphthalate, a transition that occurs when viscosity is higher than $10^{10}\,\mathrm{Pa\,s}$ [16]. The concept of free volume has been recently used [17] to interpret the variations of the viscosity with temperature of various alcohols (pentanol, heptanol, nonanol, and theirs isomers) and of vinyl acetate. These variations are not in agreement with the Arrhenius law in the temperature range 298.15 to 443.15 K. We should mention the recent work of Qun-Fang, Yu-Chun, and Rui-Sen [18] based on Eyring's model, which needs two adjustable parameters (and also vapor pressure at each temperature, saturated liquid volume, and the heat of vaporization). The viscosity is expressed as a function of energy of vaporization because they think that the bonds that must be broken during the movement of the viscous fluid are the same as those that are broken during the vaporization process. For 106 compounds and 1473 experimental data they obtain an average absolute deviation of 1.51% and the maximum deviation ($\mathcal{D}_{\rm max}$) is 11.96%. Examination of their results indicates an average absolute deviation of 4.6% for methane ($\mathcal{D}_{\rm max} = 8.73\%$), 3.6% for benzene ($\mathcal{D}_{\rm max} = 9.7\%$), 2.7% for 2-propanol ($\mathcal{D}_{\rm max} = 8.5\%$), 3.4% for water ($\mathcal{D}_{\rm max} = 8.0\%$), and 6.4% for *n*-butyric acid ($\mathcal{D}_{\rm max} = 12.0\%$). The results are good but the model is limited to saturated liquids. Mixtures were not considered in this work

Recently [19] we have proposed an approach in order to model the viscosity of Newtonian fluids (in the condensed phase; density $\rho > 200\,\mathrm{kg\,m^{-3}}$) with small molecules. This approach tried to connect dynamic viscosity η to molecular structure. This model has been tested [19,20] using a database of 41 compounds of very different chemical species: alkanes (linear and ramified, light and heavy), alkylbenzenes, cycloalkanes, alcohols, fluoroalkanes (refrigerant), carbon dioxide, and water. Unfortunately an analysis showed that for less dense fluids, i.e., the light alkanes, the results are not satisfactory enough. For example, in the case of methane, if one considers 703 points (a part of the database [20]) with $90.38 \leqslant T \leqslant 600\,\mathrm{K}$ and $0.1 \leqslant P \leqslant 200\,\mathrm{MPa}$, one obtains $\mathcal{D}_{\mathrm{av}} = 38.84\%$ and $\mathcal{D}_{\max} = 99.8\%$. This model fails because it predicts (like other models as already mentioned) a zero viscosity while density tends towards zero and this is not in agreement with the viscosity of the dilute gas. The deviations are very high at low pressures and the calculation shows that density ρ must be higher than a value of the order of about $200\ \mathrm{kg\,m^{-3}}$. For methane we obtained in this last case (274 points) $\mathcal{D}_{\mathrm{av}} = 10.65\%$ and $\mathcal{D}_{\max} = 34.3\%$. If $\rho > 300\,\mathrm{kg\,m^{-3}}$ (155 points) then $\mathcal{D}_{\mathrm{av}} = 6.29\%$ and $\mathcal{D}_{\max} = 22.06\%$. For the pressure range $P \leqslant 110\,\mathrm{MPa}$ with $\rho > 200\,\mathrm{kg\,m^{-3}}$ there are 3012 points in the database [19] and $\mathcal{D}_{\mathrm{av}} = 2.8\%$ (9.35% for methane with $\mathcal{D}_{\max} = 37.29\%$).

The basic ideas of the previous models are very general but they consider only the case of fluids in dense state. A more satisfying model should be able to represent simultaneously the dense and gaseous states and the transition from low to dense states. Although their model is not linked with the free-volume concept or Eyring's representation, in order to further compare the performances of our model with already efficient existing models, it is interesting to mention here the very recent semiempirical model of Quiñones-Cisneros, Zéberg-Mikkelsen, and Stenby [21] based on friction macroscopic concepts of classical mechanics and the van der Waals theory of fluids. This semitheoretical model describes correctly the transition from low-dense to dense states. Separating the total viscosity into a dilute gas term and a friction term, a connection between the van der Waals repulsive (p_r) and attractive (p_a) pressure terms and the viscosity friction term η_f is proposed: $\eta_f = \kappa_a p_a + \kappa_r p_r + \kappa_{rr} p_r^2$ where the kappa parameters are temperature dependent coefficients. The dynamic viscosity is $\eta = \eta_0 + \eta_f$ where η_0 is the dilute gas viscosity. The quadratic term has been introduced in order to obtain an accurate description of the viscosity for dense fluids at high pressures. This theory has been applied to some normal alkanes from methane to decane in both dense and gaseous states. With five parameters, the results they obtained are $\mathcal{D}_{\mathrm{av}} = 1.80\%$ for methane (with $0.1 \leqslant P \leqslant 69.9\,\mathrm{MPa}$), 2.51% for propane (with $0.11 \leqslant P \leqslant 55.2\,\mathrm{MPa}$), 1.92% for hexane (with $0.098 \leqslant P \leqslant 100\,\mathrm{MPa}$), 1.66% for octane (with $0.1 \leqslant P \leqslant 102.1\,\mathrm{MPa}$). They do not give the maximum deviation in their article.

We propose in the following section, to present an approach in order to model the viscosity of Newtonian fluids, based on both the free-volume concept and the diffusion models of the molecules, which is a very different point of view from the one of the [21] model. Our model tries to connect viscosity to molecular structure and to describe correctly the low-dense to dense state transition. The object of this article is on the one hand to present this model (combination of the free-volume and microscopic friction factor), and on the other hand to discuss the numerical results obtained on various compounds, focusing of course on the transition between the gas and the dense state.

PRESENTATION OF THE MODEL

Viscosity of dilute gas

In the gaseous state or low-density state, when density ρ tends towards 0, our previous model failed [19] because it indicates that viscosity also tends towards 0. That is not correct. It is well known that the viscosity of dilute gas is correctly described by the kinetic theory and that of Chapman-Enskog that forms the theoretical base of a predictive model of viscosity η_0 of dilute gas. This theory takes into account correctly the intermolecular forces at very low density. At high density, a hard-sphere system behaves like a low-density hard-sphere system except that all the events occur at a faster rate due to the higher rate of collision. That involves a correction to η_0. One possibility is known as the ''Modified Enskog Theory'' and in that theory the effective collision diameter is a function of temperature and density. Another possibility, often used, writes dynamic viscosity in the form

$$\eta = \eta_0 + \Delta\eta, \tag{2}$$

where the term $\Delta\eta$ term characterizes the passage in a dense state. Recently, such development has been used in [21–23] and further information can be found in a review book [24]. Our model deals with the additional term $\Delta\eta$ and uses η_0 from already existing models.

The model of Chung *et al.* [25] modifies the Chapman-Enskog theory to characterize the effects of molecular shape and anisotropic molecular forces. It can be used to evaluate η_0 and gives, viscosity expressed in micropoise, $\eta_0 = 40.785(\sqrt{MT}/V_c^{2/3}\Omega^*)F_c$ where the following empirical equations are used to evaluate the reduced integral of collision:

$$\begin{aligned}\Omega^* = {} & \frac{1.16145}{T^{*0.14874}} + \frac{0.52487}{\exp(0.77320T^*)} \\ & + \frac{2.16178}{\exp(2.43787T^*)} \\ & - 6.435\times10^{-4}T^{*0.14874}\sin(18.0323T^{*-0.76830} \\ & - 7.27371)\end{aligned}$$

with $T^* = 1.2593T/T_c$. In η_0 the critical volume V_c is in $\mathrm{cm^3mol^{-1}}$ and the factor F_c is empirically estimated by $F_c = 1 - 0.2756\omega$ where ω is the acentric factor (at least for the nonpolar gases presented here). It is necessary to know the critical physical constants of the studied systems.

Relation between viscosity and microstructure

When a fluid is sheared with a rate $\dot{\gamma}(t)$ (t is the time) the viscosity is defined by the ratio $\eta = \sigma(t)/\dot{\gamma}(t)$ where $\sigma(t)$ is the shear stress. For a Newtonian fluid this ratio is time independent. The shear stress is a function of the linear viscoelastic properties of a material as expressed by the Boltzmann constitutive equation $\sigma(t) = \int_{-\infty}^{t} G(t-t')\,\dot{\gamma}(t')\,dt'$ where $G(t)$ is the relaxation function of the fluid. For a constant shear rate one obtains $\eta=\int_0^\infty G(t)dt$. It is thus sufficient to know the relaxation function $G(t)$ to determine the dynamic viscosity η. Among the many models of $G(t)$, the dumbbell model and generalized dumbbell models make it possible to connect viscosity to the microstructure. In the dumbbell model the molecule is described by spheres connected by a spring. The molecule moves in a fluid containing identical molecules of molar mass M. On each sphere are exerted the viscous friction forces associated to Stokes's law and the spring force. The assessment of the forces leads to the relaxation function $G(t)=(\rho RT/M)\exp(-t/\tau_H)$ where τ_H is the average time necessary for the molecule to change its conformation and where R is the perfect gas constant. It is the characteristic relaxation time and it is given by $\tau_H=\zeta b^2/(12kT)$ where b^2 is the average quadratic length of the spring and ζ the friction coefficient of the sphere associated to the dumbbell. The friction coefficient ζ is related to the mobility of the molecule and to the diffusion process (diffusion of the momentum for viscosity). Then $\eta=\int_0^\infty G(t)dt=\rho N_a\zeta b^2/(12M)$, where N_a is the Avogadro number. In the generalized model (or Rouse model for polymer [26]), a molecule is considered as a succession of N dumbbells (length b) joined to each other and able to take different orientations. Calculation leads to $G(t)=(\rho RT/M)\Sigma_{p=1}^{\infty}\exp(-tp^2/\tau_R)$ with $\tau_R=\zeta b^2N^2/(6\pi^2kT)$ for large N. The integration of $G(t)$ provides $\eta=\rho N_a\zeta b^2N^2/(36M)$ (see, for instance, [27]). In both cases one can write that the viscosity in the dense state is in the form

$$\Delta\eta=\frac{\rho N_a\zeta L^2}{M} \tag{3}$$

where L appears as an average quadratic length. For a linear molecule, calculations shows that $L^2=\langle r^2\rangle N/36$ where $\langle r^2\rangle$ is the mean quadratic end to end distance of the molecule. For a spherical molecule $L^2=3\langle r^2\rangle/5$. The interested reader will find a more detailed presentation of these known results, especially used for liquid polymers, in a reference work [28].

Free volume

The free-volume fraction f_v is characteristic of the empty space between molecules. Using the Doolittle [9] Eq. (1) we assume

$$\Delta\eta=A\exp(B/f_v) \tag{4}$$

where B (which is positive) is characteristic of the free-volume overlap. It is important to recall that this relation has been theoretically justified [8,29] for the molecular transport in liquids and glasses. We choose $f_v=v_f/v$ as the free-volume fraction (v is the specific molecular volume, v_0 is molecular volume of reference or hard volume, and $v_f=v-v_0$) definition used, for example, by [11,12,30]. It is interesting to point out here that alternatively f_v may be defined as v_f/v_0 as pointed out by [10,12]. A simple calculation shows that the form of the Doolittle's equation does not change using this definition. Using the fluctuation-dissipation theory of the free volume, the free volume v_f can be written [30] in the form $v_f=(4kT/k_a)^{3/2}$ where k_a is the stiffness of the background. To calculate this stiffness it is necessary to make two assumptions: The molecule is in a state such that the molecular potential energy of interaction with its neighbors is E/N_a (N_a is Avogadro's number); The mean displacement of the molecule is b_d such that $b_d^3\propto v$ (total volume of the molecule). Notice here that in the low-density state $b_d\to\infty$ and that in the high-density state $b_d^3\to v_0$.

Under these conditions the stiffness k_a is defined by $\frac{1}{2}k_ab_d^2=E/N_a$. This gives $v_f=b_d^3(2RT/E)^{3/2}$, i.e., $v_f\propto v(2RT/E)^{3/2}$ and thus the free-volume fraction is defined by

$$f_v\propto\left(\frac{RT}{E}\right)^{3/2} \tag{5}$$

We assume that $E=E_0+PM/\rho$ (P is the pressure) where the term $PM/\rho=PV$ is connected to the energy necessary to form the vacant vacuums available for the diffusion of the molecules and where E_0 is connected to the barrier energy that the molecule must cross to diffuse. R is the gas constant.

The coefficient of friction and viscosity

Using the combination of Eqs. (3) and (4) leads to write ζ in the form

$$\zeta=\zeta_0\exp(B/f_v) \tag{6}$$

and thus

$$\Delta\eta=\frac{\rho N_aL^2\zeta_0\exp(B/f_v)}{M} \tag{7}$$

It is possible to determine the quantity ζ_0, which is the value of the friction coefficient when $f_v\gg B$. For a molecule we already indicated that the potential energy is E/N_a. We assume that this energy is dissipated by a friction force F defined by the relation $F=\zeta_0\overline{\nu}$ where $\overline{\nu}$ is the molecular velocity. This dissipation corresponds to a length b_f. But $(E/N_a)=b_f\zeta_0\overline{\nu}$. Assuming that all the thermal energy of activation is transformed into kinetic energy, $\frac{3}{2}kT=\frac{1}{2}(M/N_a)\overline{\nu}^2$, i.e., $\overline{\nu}^2=(3RT/M)$. By combining these relations [31],

$$\zeta_0=\frac{E}{N_ab_f}\left(\frac{M}{3RT}\right)^{3/2}, \tag{8}$$

where b_f is the dissipation length of the energy E.

The viscosity

Combining Eqs. (5), (7), and (8) one obtains the expression

$$\eta=\eta_0+\frac{\rho l\left(E_0+\dfrac{PM}{\rho}\right)}{\sqrt{3RTM}}\exp\left[B\left(\frac{E_0+\dfrac{PM}{\rho}}{RT}\right)^{1/2}\right] \tag{9}$$

where $l=L^2/b_f$ is homogeneous with a length. Moreover, as already indicated, in the expression of energy E, the term $PV=PM/\rho$ is linked to the energy necessary to form the vacant vacuums available for the diffusion of the molecules and the term E_0 is connected to the barrier of energy that a molecule must cross to diffuse. In the dense state, for a small density variation, at first approximation E_0 is almost constant. However, this is not valid any more for the dilute state for which it seems normal to admit that $E_0 \rightarrow 0$ when $\rho \rightarrow 0$, as there are no more interactions between the molecules in the system. Therefore, E_0 is expressed as $E_0=\alpha\rho$ and Eq. (9) is then modified as follows:

$$\eta=\eta_0+\frac{\rho l\left(\alpha\rho+\dfrac{PM}{\rho}\right)}{\sqrt{3RTM}}\exp\left[B\left(\frac{\alpha\rho+\dfrac{PM}{\rho}}{RT}\right)^{3/2}\right] \tag{10}$$

We mention here that in the very well-known statistical thermodynamic model of fluids developed by Flory, Orwoll, and Vrij [32], the potential energy of interaction of a molecule is given by $E_0 \propto 1/v$, i.e., $E_0 \propto \rho$, an assumption similar to our hypothesis. Moreover, if $\rho \rightarrow 0$ then $E=\alpha\rho+PM/\rho \rightarrow RT$ and $f_v \rightarrow 1$ in agreement with the definition $f_v=v_f/v$. Hence, the coefficient factor in Eq. (5) is equal to unity. One sees that Eq. (10) involves the three parameters l, α, and B that are characteristic of the considered molecule.

DATABASE AND CHARACTERISATION OF THE RESULTS

The main purpose of this paper is to show that this viscosity theory is applicable to all states and is able to cover the entire low- to high-pressure range. So, in a first step we used a database built up on the basis of methane and propane, in the gaseous and dense states. For methane (CH_4, $M=16.043\,\mathrm{g\,mol^{-1}}$) [33] we have considered 885 data points in the pressure and temperature intervals $0.01 \leqslant P \leqslant 200$ MPa and $90.7 \leqslant T \leqslant 600$ K. For propane (C_3H_8, $M=44.096\,\mathrm{g\,mol^{-1}}$) [22] there are 1085 data points in the pressure and temperature intervals $0.01 \leqslant P \leqslant 100$ MPa and $90 \leqslant T \leqslant 600$ K. In a second step we have considered such substances as follows: hexane (C_6H_{14}, $M=86.177\,\mathrm{g\,mol^{-1}}$) (Refs. [34–36], 292 data points, $0.1 \leqslant P \leqslant 250.02$ MPa and $273.15 \leqslant T \leqslant 423.5$ K); octane (C_8H_{18}, $M=114.230\,\mathrm{g\,mol^{-1}}$) (Refs. [34, 37–39], 347 data points, $0.1 \leqslant P \leqslant 505.5$ MPa and $273.15 \leqslant T \leqslant 448$ K); dodecane ($C_{12}H_{26}$, $M=170.337\,\mathrm{g\,mol^{-1}}$) (Refs. [37,38], 53 data points, $0.1 \leqslant P \leqslant 501.6$ MPa and $298.15 \leqslant T \leqslant 373.21$ K); trans-decaline ($C_{10}H_{18}$, $M=136.252\,\mathrm{g\,mol^{-1}}$) (Ref. [6], 51 data points and $0.1 \leqslant P \leqslant 360$ MPa and $288.71 \leqslant T \leqslant 388.15$ K): benzene (C_6H_6, $M=78.113\,\mathrm{g\,mol^{-1}}$) (Refs. [40,41], 56 data points and $0.1 \leqslant P \leqslant 402.2$ MPa and $298.38 \leqslant T \leqslant 373.17$ K), which are generally in the dense state (some data points at low pressure and high temperature are in the gaseous state) but for which the pressure reaches 505.5 MPa, in order to verify also our model at very high pressures. We have also considered the case of the 2,2-dimethylpropane (C_5H_{12}, $M=72.150\,\mathrm{g\,mol^{-1}}$) (Ref. [42], 94 data points and $7 \leqslant P \leqslant 56$ MPa and $311 \leqslant T \leqslant 444$ K) because in the previous analysis for dense fluids [19] its representation was bad ($\mathcal{D}_{\mathrm{av}}=3.27\%$ and $\mathcal{D}_{\mathrm{max}}=40.93\%$). For these six compounds the total number of data points is 903.

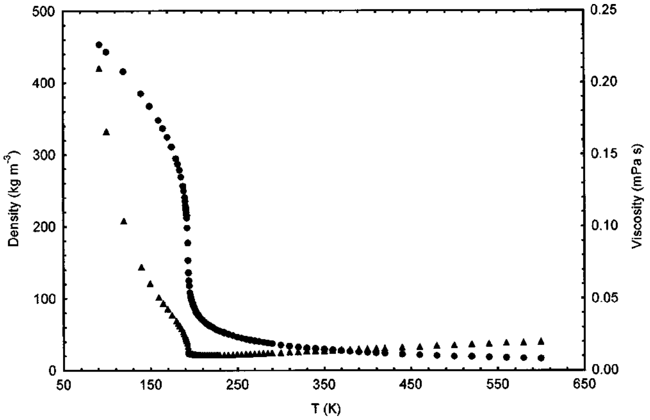

FIG. 1. Variations versus T at $P=5$ MPa, of the literature (Ref. [33]) methane dynamic viscosity (▲) and density (●).

In order to evaluate the performances of this model it is necessary to introduce quantities characteristic of the results obtained. η_{exp} is the experimental value of viscosity and η_{cal} the value calculated using the model. For each point we define the following quantities, where D is the deviation and $\mathcal{D}$ is the absolute deviation:

$$D=100(1-\eta_{\mathrm{cal}}/\eta_{\mathrm{exp}})\quad(\%)$$

$$\mathcal{D}=|D|\quad(\%).$$

These quantities are expressed as percentages. For all the points considered we define the three following characteristic quantities (N_b is the total number of experimental points),

$$\mathcal{D}_{\mathrm{av}}=\frac{1}{N_b}\sum_{i=1}^{i=N_b}\mathcal{D}(i)$$

$$\mathcal{D}_{\mathrm{max}}=\mathrm{Max}[\mathcal{D}(i)]$$

$$\mathcal{B}=\frac{1}{N_b}\sum_{i=1}^{i=N_b}D(i)$$

The average absolute deviation ($\mathcal{D}_{\mathrm{av}}$) characterizes the fact that the experimental points are more or less close to the calculated curve. The average deviation or Bias ($\mathcal{B}$) characterizes the quality of the distribution of the experimental points on either side of the calculated curves. If $\mathcal{D}_{\mathrm{av}}=\mathcal{B}$ then all the experimental points are above the calculated curves. If $\mathcal{D}_{\mathrm{av}}=-\mathcal{B}$ then all the experimental points are below the calculated curves. Finally $\mathcal{D}_{\mathrm{max}}$ characterizes the maximum deviation produced by the model.

RESULTS OF THE NUMERICAL ANALYSIS

For methane, Fig. 1 shows the variations versus temperature at $P=5$ MPa, on the same graph of the dynamic viscos-

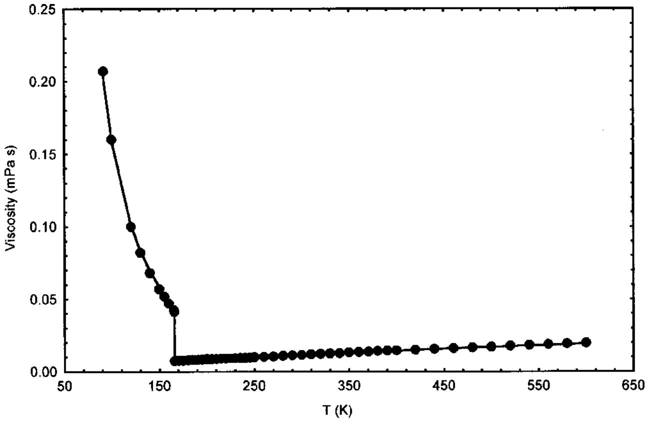

FIG. 2. Variations of the methane dynamic viscosity versus T at $P=2$ MPa. (●, experimental; ——, calculated curve.)

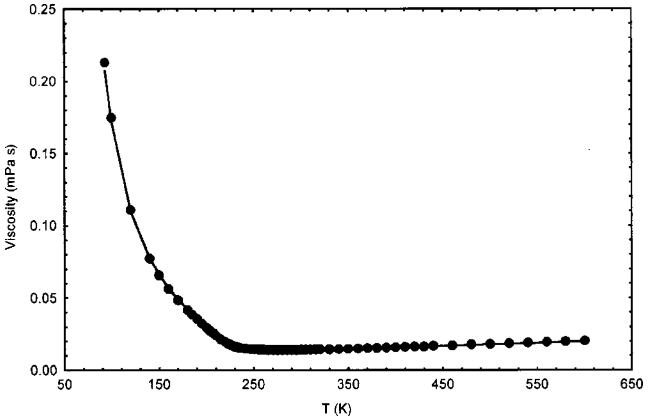

FIG. 4. Variations of the methane dynamic viscosity versus T at $P=10$ MPa. (●, experimental; ——, calculated curve.)

ity and density. This figure shows that there is no obvious relationship between dynamic viscosity and density. For methane we have obtained $D_{\mathrm{av}}=2.59\%$, $\mathcal{D}_{\max}=14.8\%$ (at $P=200\,\mathrm{MPa}$ and $T=300\,\mathrm{K}$) and $\mathcal{B}=1.02\%$ with $l=0.590\,803\,\text{Å}$, $\alpha=37.8049\,\mathrm{J\,mol^{-1}\,m^{3}\,kg^{-1}}$, and $B=9.002163\times10^{-3}$. Figures 2–5 show the variations of dynamic viscosity versus temperature at, respectively, $P=2$, 5 (see also Fig. 1), 10, and 100 MPa. Note here that for methane the critical point is at $P_c=4.63\,\mathrm{MPa}$ and $T_c=190.7\,\mathrm{K}$. Figure 6 shows the variations of the deviation at $P=5$ MPa (close to the critical pressure) versus temperature (see also Fig. 3). Figures 7–9 show the variations of dynamic viscosity versus pressure at, respectively, $T=190$ (close to critical temperature), 150, and 300 K. In Fig. 7 the circles are experimental points used for the fitting and the triangles are experimental points that were not used for the fitting (there are thousands points concerning the dynamic viscosity of methane in Ref. [32]). It is very interesting to notice that these points are very near the calculated curve and the curvature between 2 and 5 MPa is very well estimated. For this isotherm $D_{\mathrm{av}}=1.78\%$ and $\mathcal{D}_{\max}=4.98\%$ (at $P=4$ MPa), including also the triangle points. In the case of Fig. 8, below $P=1$ MPa there are in fact several points in the gaseous state (not seen on the figure). We made also a calculation considering only the values restricted to $0.1\leqslant P\leqslant200\,\mathrm{MPa}$ and $\rho\geqslant200\,\mathrm{kg\,m^{-3}}$, as was considered in the previous work for dense fluids [19]. We obtained $\mathcal{D}_{\mathrm{av}}=2.69\%$, $\mathcal{D}_{\max}=9.31\%$, and $\mathcal{B}=0.64\%$ with the new equation (10) instead of $\mathcal{D}_{\mathrm{av}}=11.18\%$, $\mathcal{D}_{\max}=33.7\%$, and $\mathcal{B}=1.41\%$ with the model valid only for dense fluids.

In the case of propane (critical point at $P_c=4.25\,\mathrm{MPa}$ and $T_c=369.7\,\mathrm{K}$) we obtained $\mathcal{D}_{\mathrm{av}}=2.50\%$, $\mathcal{D}_{\max}=9.19\%$ (at $P=40\,\mathrm{MPa}$ and $T=600\,\mathrm{K}$) and $\mathcal{B}=-0.95\%$ with $l=0.847825\,\text{Å}$, $\alpha=59.4963\,\mathrm{J\,mol^{-1}\,m^{3}\,kg^{-1}}$, and $B=7.392\times10^{-3}$. Figures 10 and 11 represent the variations of dynamic viscosity versus temperature near the critical pressure, at $P=4$ MPa in normal and logarithmic scales (in order to see the variations near the critical point). Figures 12 and 13 represent the variations of dynamic viscosity versus pressure at $T=160$ and 370 K. Figure 13 shows that, even at $T=370\,\mathrm{K}$ very close to the critical isotherm ($T_c=369.7\,\mathrm{K}$), the model still gives a good performance.

In both cases the results are good in dense and gaseous state. Notice that for methane the claimed experimental accuracy is 2% except in the critical region where it is 5%, and for propane the accuracy is 0.4% in the dilute gas region, 2.5% up to 30 MPa and $100\leqslant T\leqslant475\,\mathrm{K}$, and 4% outside this range. The model is able to represent the gas-liquid transition

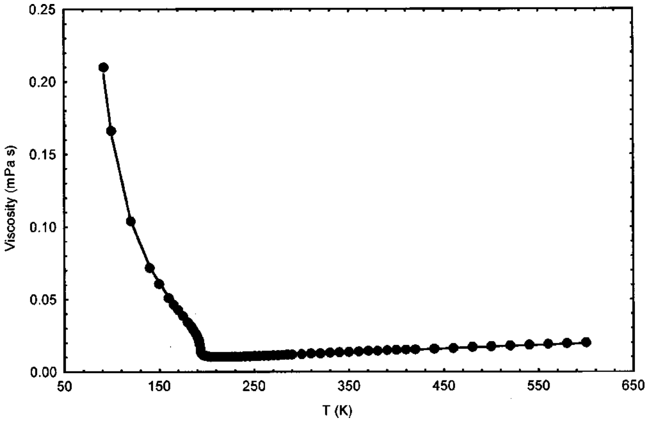

FIG. 3. Variations of the methane dynamic viscosity versus T at $P=5$ MPa. (●, experimental; ——, calculated curve.)

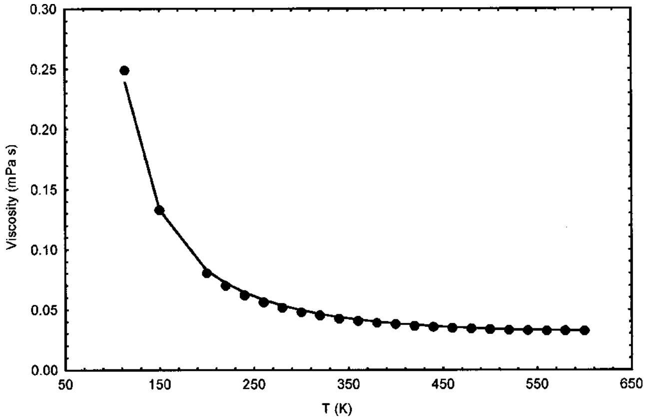

FIG. 5. Variations of the methane dynamic viscosity versus T at $P=100$ MPa. (●, experimental; ——, calculated curve.)

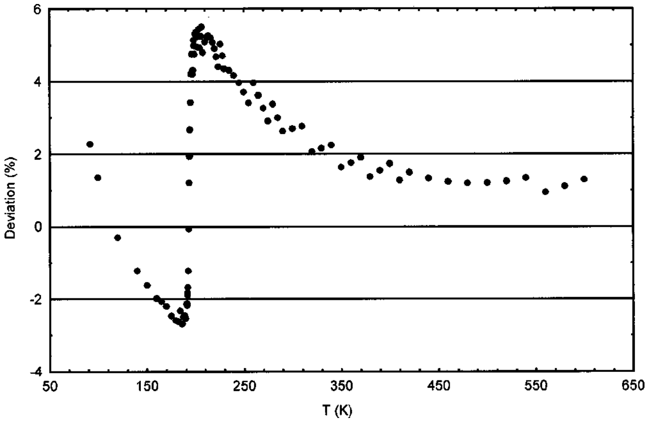

FIG. 6. Variations of the deviation at $P = 5$ MPa versus T for the methane dynamic viscosity.

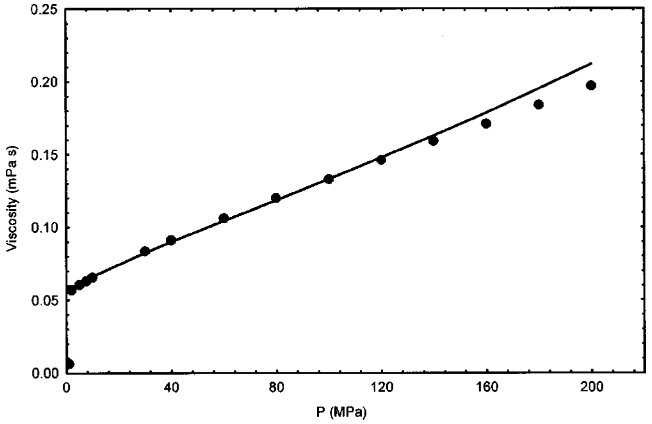

FIG. 8. Variations of the methane dynamic viscosity versus P at $T = 150$ K. (●, experimental; ——, calculated curve.)

and the behavior in the supercritical conditions. It is possible to improve the values of $\mathcal{D}_{\mathrm{av}}$ putting a corrective factor $(1 + cP)/(1 + dT)$ in front of the $\Delta\eta$ expression. For methane we obtained with five parameters $\mathcal{D}_{\mathrm{av}} = 0.99\%$, $\mathcal{D}_{\max} = 16.76\%$, and $\mathcal{B} = 0.53\%$ and for propane $D_{\mathrm{av}} = 1.97\%$, $\mathcal{D}_{\max} = 16.18\%$, and $\mathcal{B} = -0.42\%$. This corrective term might be representative of possible variations of the l term versus pressure and temperature (we have obtained for methane $c = -1.98143 \times 10^{-9}\ \mathrm{Pa}^{-1}$ and $d = 3.96467 \times 10^{-4}\ \mathrm{K}^{-1}$ and for propane $c = 2.16703 \times 10^{-9}\ \mathrm{Pa}^{-1}$ and $d = 3.19811 \times 10^{-4}\ \mathrm{K}^{-1}$).

For the other compounds Eq. (10) gives the following results.

(1) For benzene (56 data points up to 402.2 MPa) we obtained $\mathcal{D}_{\mathrm{av}} = 0.72\%$, $\mathcal{D}_{\max} = 6.56\%$ (at $P = 402.2$ MPa and $T = 373.17$ K), and $\mathcal{B} = 0.70\%$. It should be pointed out that the maximum deviation occurs at the highest pressure for which there is only one experimental point (only for $T = 373.17$ K), which may explain a bad precision of the fitting procedure in this region. It is generally the same for the other compounds (there are few points at the highest pressures).

(2) For hexane (292 data points up to 250 MPa with 9 points in gaseous state at $P = 0.1$ MPa) we obtained $\mathcal{D}_{\mathrm{av}} = 1.09\%$, $\mathcal{D}_{\max} = 6.50\%$ (at $P = 249.2$ MPa and $T = 303.15$ K), and $\mathcal{B} = 0.07\%$.

(3) For trans-decaline (51 data points up to 360 MPa) we obtained $\mathcal{D}_{\mathrm{av}} = 2.03\%$, $\mathcal{D}_{\max} = 8.34\%$ (at $P = 0.1$ MPa and $T = 288.7$ K), and $\mathcal{B} = -0.37\%$.

(4) For octane (347 data points up to 505.5 MPa with 3 points in gaseous state at $P = 0.1$ MPa) we obtained $\mathcal{D}_{\mathrm{av}} = 2.51\%$, $\mathcal{D}_{\max} = 19.6\%$ (at $P = 503$ MPa and $T = 348.29$ K), and $\mathcal{B} = 0.53\%$.

(5) For 2,2-dimethylpropane (94 data points up to 56 MPa) we obtained $\mathcal{D}_{\mathrm{av}} = 3.23\%$, $\mathcal{D}_{\max} = 15.6\%$ ($P = 5.6$ MPa and $T = 444.26$ K), and $\mathcal{B} = 1.49\%$. Notice in that case the improvement of the representation ($\mathcal{D}_{\mathrm{av}} = 3.27\%$ but $\mathcal{D}_{\max} = 40.93\%$, and $\mathcal{B} = -1.38\%$ with the previous model).

(6) For dodecane (53 data points up to 501.6 MPa) we obtained $\mathcal{D}_{\mathrm{av}} = 3.51\%$, $\mathcal{D}_{\max} = 18.5\%$ (at $P = 501.6$ MPa and $T = 373.21$ K), and $\mathcal{B} = -1.40\%$.

As an illustration, Fig. 14 shows the variations of the dynamic viscosity of hexane versus T at $P = 0.1$ MPa, where hexane is either in gaseous or liquid state, depending on the value of temperature (boiling point at 341.9 K). Figure 15 shows the curve corresponding to the experimental dynamic viscosity versus calculated dynamic viscosity for hexane. The line is practically the bisectrix line. Figure 16 shows the

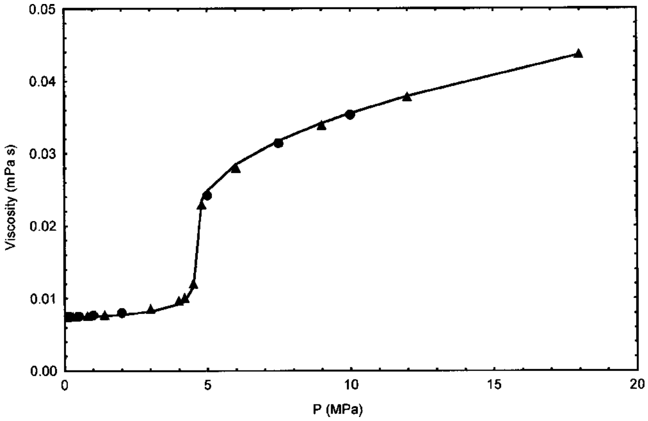

FIG. 7. Variations of the methane dynamic viscosity versus P at $T = 190$ K. (●, experimental points used for the fitting; ▲, experimental points not used for the fitting; ——, calculated curve.)

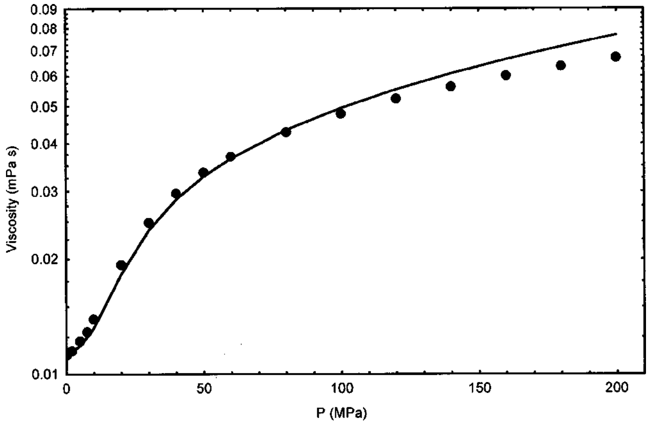

FIG. 9. Variations of the methane dynamic viscosity versus P at $T = 300$ K. (●, experimental; ——, calculated curve.)

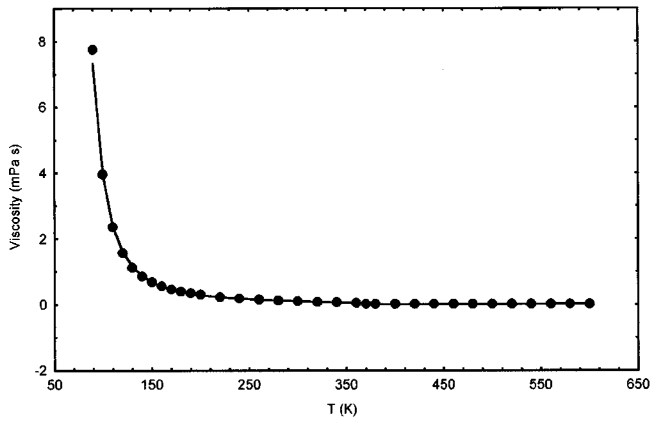

FIG. 10. Variations of the propane dynamic viscosity versus T at $P=4$ MPa. (●, experimental; ——, calculated curve.)

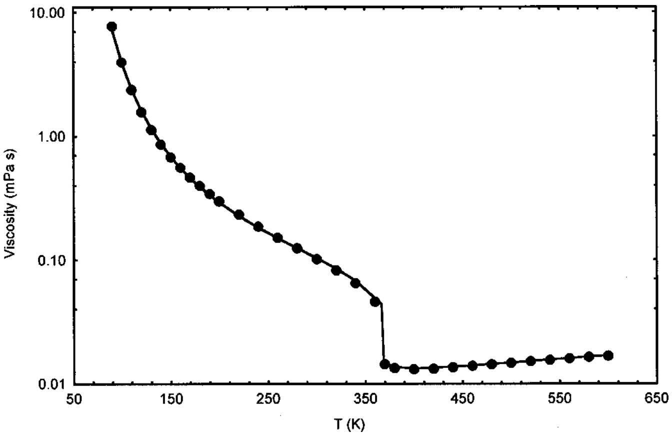

FIG. 11. Variations of the propane dynamic viscosity versus T at $P=4$ MPa. (logarithmic scale) (●, experimental; ——, calculated curve.)

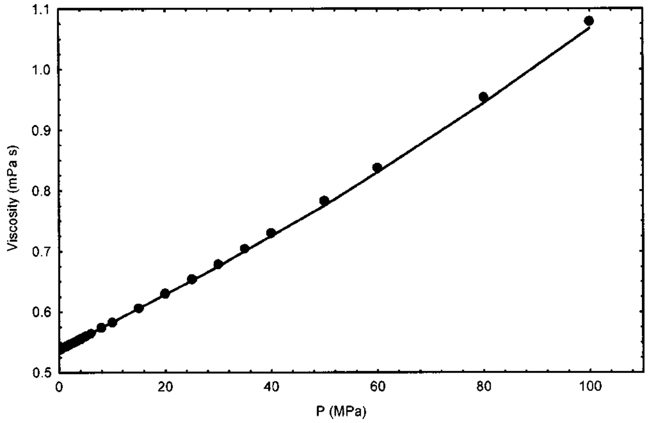

FIG. 12. Variations of the propane dynamic viscosity versus P at $T=160$ K. (●, experimental; ——, calculated curve.)

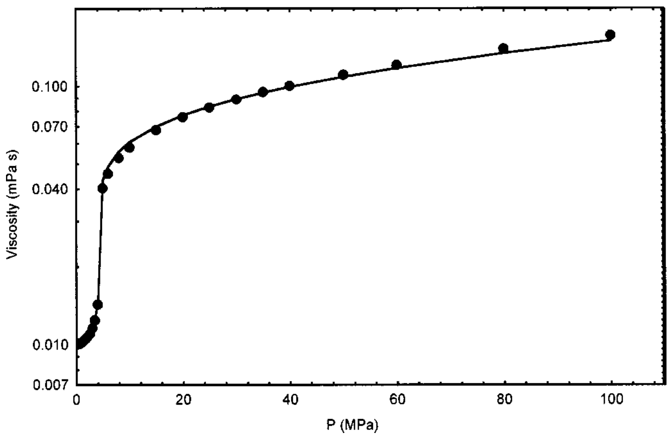

FIG. 13. Variations of the propane dynamic viscosity versus P at $T=370$ K. (●, experimental; ——, calculated curve).

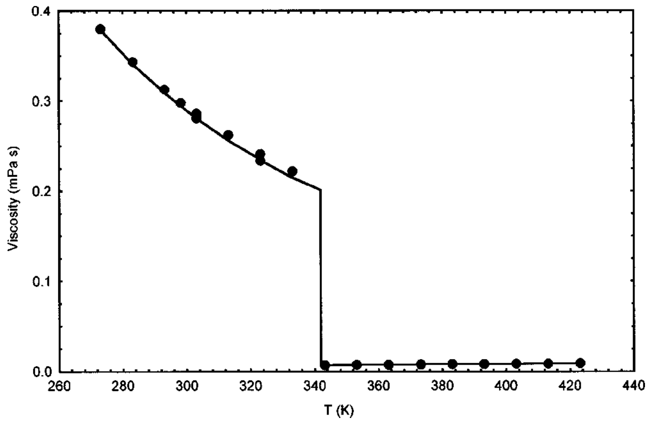

FIG. 14. Variations of the hexane dynamic viscosity versus T at $P=0.1$ MPa. (●, experimental; ——, calculated curve).

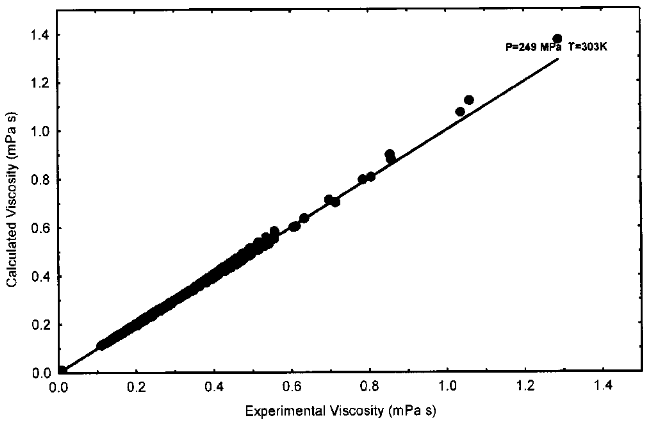

FIG. 15. Experimental hexane dynamic viscosity versus calculated dynamic viscosity. (——, bisectrix line).

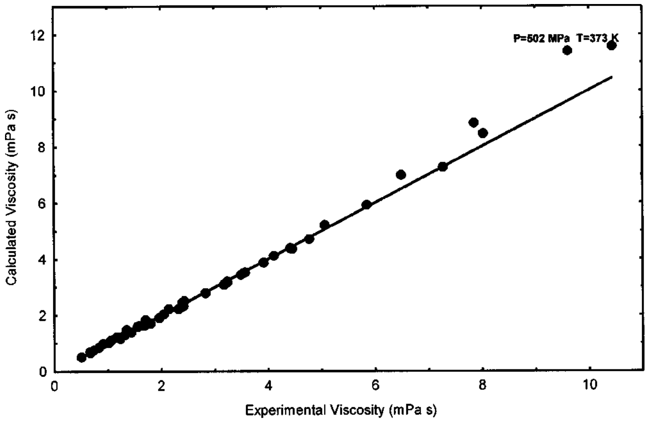

FIG. 16. Experimental dodecane dynamic viscosity versus calculated dynamic viscosity. (——, bisectrix line.)

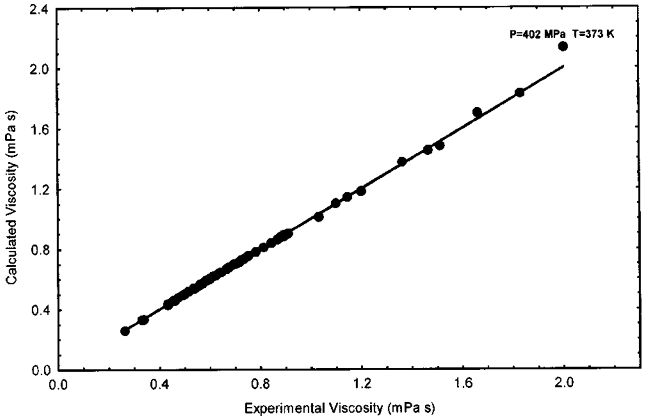

FIG. 17. Experimental benzene dynamic viscosity versus calculated dynamic viscosity. (——, bisectrix line.)

same curve in the case of the dodecane, which is the worst case for $\mathcal{D}_{\mathrm{av}}(3.51\%)$ and for which the experimental accuracy is 2%. We mention here that for $\mathcal{D}_{\max}$, the worst case is octane for which the experimental accuracy is 2–3 % ($\mathcal{D}_{\max}=19.6\%$ with $D_{\mathrm{av}}=2.51\%$), but with our previous model in the liquid state (so excluding the points in the gaseous state) $\mathcal{D}_{\mathrm{av}}=4.82\%$ and $\mathcal{D}_{\max}=31.14\%$. Figure 17 is related to benzene, which is the best case. The points with the maximum deviation are indicated on the figures with the corresponding coordinates. Finally the use of a correction factor for $\Delta\eta$ improves the results. For instance, with five parameters, for benzene $\mathcal{D}_{\max}$ is 3.94% (instead of 6.50% with three parameters), the value of $\mathcal{D}_{\mathrm{av}}=1.06\%$ (instead of 1.09%) being nearly the same. For octane we obtained $\mathcal{D}_{\mathrm{av}}=1.78\%$ and $\mathcal{D}_{\max}=17.4\%$ with five parameters instead of 2.51% and 19.63% with three parameters.

As already pointed out it is interesting to compare here our results with the very recent model of Quiñones-Cisneros, Zéberg-Mikkelsen, and Stenby [21] based on friction macroscopic concepts of classical mechanics and the van der Waals theory of fluids. This theory has been applied to some alkanes from methane to decane in both dense and gaseous states. With five parameters, the results they obtained are $\mathcal{D}_{\mathrm{av}}=1.80\%$ for methane (with $0.1\leqslant P\leqslant 69.9\,\mathrm{MPa}$), 2.51% for propane (with $0.11\leqslant P\leqslant 55.2\,\mathrm{MPa}$), 1.92% for hexane (with $0.098\leqslant P\leqslant 100\,\mathrm{MPa}$), 1.66% for octane (with $0.1\leqslant P\leqslant 102.1\,\mathrm{MPa}$). They do not give the maximum deviation in their article. Our results, with three parameters, extended to much higher pressures and based on a very different point of view are comparable to theirs. Moreover, for methane, if we restrict to $P\leqslant 70\,\mathrm{MPa}$ we obtain $\mathcal{D}_{\mathrm{av}}=2.02\%$ and $\mathcal{D}_{\max}=5.71\%$ (at $T=250\,\mathrm{K}$ and $P=10\,\mathrm{MPa}$) with the three parameters previously determined without restriction on P (P up to 200 MPa). A new fitting with $P\leqslant 70\,\mathrm{MPa}$ gives $\mathcal{D}_{\mathrm{av}}=1.39\%$ and $\mathcal{D}_{\max}=8.17\%$ (at $T=105\,\mathrm{K}$ and $P=60\,\mathrm{MPa}$). For octane, if we restrict to $P\leqslant 104\,\mathrm{MPa}$ we obtain $\mathcal{D}_{\mathrm{av}}=2.25\%$ and $\mathcal{D}_{\max}=15.2\%$ (at $T=448\,\mathrm{K}$ and $P=19.4\,\mathrm{MPa}$) with the three parameters previously determined without restriction on P (P up to 505.5 MPa). A new fitting with $P\leqslant 104\,\mathrm{MPa}$ gives $\mathcal{D}_{\mathrm{av}}=1.56\%$ and $\mathcal{D}_{\max}=15.2\%$ (still at $T=448\,\mathrm{K}$ and $P=19.4\,\mathrm{MPa}$).

CONCLUSION

This model, based on the relation between free volume, friction coefficient, and viscosity, seems to be quite representative of the variations of the dynamic viscosity versus pressure and temperature in both the low-density and dense states. It takes very correctly into account the transition between gas and liquid. It seems to be applicable from very low pressures (around 0.01 MPa) to high pressures (up to 500 MPa) for various chemical compounds. It involves only three parameters characteristic of the considered compound. This model emphasizes the relation between microstructure, dynamic viscosity, and free volume in the understanding of such a complex property as dynamic viscosity. It is now necessary to study the possibility of extending the model to the mixtures and to other properties. For instance, the application to self-diffusion coefficient D is obvious as it is well known that $D=kT/\zeta$ and following Eq. (6) it follows that $D\propto\exp(-\mathcal{B}/f_v)$ (see also the theoretical Ref. [8]). In a future work the relationship between free volume, dynamic viscosity, and self-diffusion coefficient will be considered.

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