

Extended Hard-Sphere Model for the Viscosity of Dense Fluids

Fausto Ciotta,¹ J. P. Martin Trusler,^{*1} and Velisa Vesovic²

- ¹ Department of Chemical Engineering, Imperial College London, South Kensington Campus, London SW7 2AZ, United Kingdom.
- ² Department of Earth Science and Engineering, Imperial College London, South Kensington Campus, London SW7 2AZ, United Kingdom.

* To whom correspondence should be addressed. E-mail: m.trusler@imperial.ac.uk

Abstract

An extended hard-sphere model is reported that may be applied to correlate and predict the viscosity of gases, liquids and supercritical fluids. The method is based on the hard-sphere model of Dymond and Assael and uses their roughness factors and molar core volumes to relate reduced viscosity to a universal function of reduced volume. The extended model behaves correctly in the limit of low densities and offers improved accuracy at high densities. The new universal reference function was determined from a large database of experimental viscosities for alkanes extending up to reduced densities of 0.84. It has been tested by correlating the viscosity of two high-viscosity liquids not used in the development of the universal function and shown to perform satisfactorily up to reduced densities of approximately 0.9.

Keywords

Alkanes; Correlation; Hard-Sphere Theory; High Pressure; Liquid; Viscosity.

Introduction

Viscosity is an important transport property from a technological point of view and plays an essential part in the calculation of fluid flow through conduits of all kinds. There is a strong economic case for developing the means to estimate viscosity accurately and reliably. For a number of simple, pure fluids correlations of critically evaluated experimental data are available. However, relying on experimental means alone is not sufficient. For engineering purposes, models are required that can predict the viscosity of fluids, including mixtures, as a function of temperature, pressure and composition. Thus one needs to develop generic, predictive models that have some basis in the underlying physical theory and that are valid for a plethora of different fluids at different conditions.

This requirement can be satisfied rigorously only for gases at low densities, where kinetic theory provides the necessary link between molecular and transport properties and the Chapman-Enskog solution of the Boltzmann equation is valid [1]. Under such conditions it is possible to predict accurately the viscosity of a number of simple gases with accuracy that is commensurate with the best experimental data [2-6]. No rigorous and complete theory exists for dense fluids, as the general solution of the Boltzmann equation is not available. The only tractable solutions developed to date are based on assuming that the molecules interact as hard spheres and that their collisions are uncorrelated. The resulting Enskog equation for the viscosity of a dense hard-sphere fluid has formed the basis for several semi-theoretical approaches, two of which in particular have found practical application: the Dymond and Assael (DA) approach [7-11] and the Vesovic-Wakeham (VW) model [12-16]. Underlying these approaches is the idea that the transport properties of real dense fluids are dominated by repulsive interactions between molecules and may be related to those of an equivalent hard-sphere fluid. The Enskog equation features in these models as an approximation for the viscosity of the equivalent hard-sphere fluid, and the two models differ in the way that they address the limitations of this equation. The present work is related to the DA approach and had the objective of extending the range of densities over which that method may be applied reliably in the correlation of viscosity for pure fluids. This work is however also related to the VW approach in the following way. The VW approach, in its simplest form [12-14], seeks to relate the viscosity of an arbitrary mixture to the viscosity of each individual component at the temperature and density of interest and, for that purpose, accurate correlations of pure-fluid viscosities are required. A current limitation of the VW model can be traced to the lack of correlative models that apply at very high densities which the present extension of the DA model will help address. More generally, the DA approach can be useful as a predictive tool for mixtures in its own right, at least for those containing molecules from within a single homologous series [9].

In the remainder of this article we first detail the original DA approach for the correlation of pure-fluid viscosity; we then introduce an extended hard-sphere model based on the excess viscosity as a means of ensuring correct behaviour in the limit of low density; finally we describe the development and testing of a new universal reference function for excess viscosity.

The Hard-Sphere Model

The hard-sphere model for the transport properties of dense fluids was proposed by Dymond [17, 18], and refined into a practical predictive tool by Dymond, Assael and their collaborators [7-11]. In the smooth-hard-sphere model, all thermodynamic and transport properties are athermal and may be conveniently expressed as functions of the reduced volume $V^* = V_m/V_0$, where V_m is the molar volume, $V_0 = N_A\sigma^3/\sqrt{2}$ is the molar volume for close-packed hard spheres, N_A is Avagadro's constant and σ is the diameter of the molecules. It is also convenient to work in terms of reduced transport coefficients and, in the DA approach, the reduced viscosity η^* was defined as follows:

$$\eta^* = (\eta / \eta_0)(V_m / V_0)^{2/3}, \quad (1)$$

where η_0 is the viscosity of the same system in the dilute-gas limit. Neglecting higher-order correction factors, $\eta_0 = (5/16\sigma^2)(mk_B T / \pi)^{1/2}$, where m is the mass of one molecule, and k_B is Boltzmann's constant. Thus the full expression for η^* is

$$\eta^* = (16/5)(2N_A)^{1/3}(\pi / MRT)^{1/2}V_m^{2/3}\eta, \quad (2)$$

where M is the molar mass and R the gas constant. In principle, the reduced viscosity η^* of smooth hard spheres can be determined as a function of V^* by molecular simulation. Indeed, the approach initially used to determine $\eta^*(V^*)$ was to combine the Enskog approximation for the viscosity of smooth hard spheres with a correction derived from molecular dynamics calculations [17].

To apply the smooth hard sphere model to systems of real spherical molecules, it is noted that, at sufficiently high densities, the thermophysical properties of liquids and supercritical fluids are dominated by repulsive interactions and can be mapped approximately on to those of the hard-sphere model if the reducing volume V_0 is treated as a weakly temperature-dependent parameter. Thus, having established the universal function $\eta^*(V^*)$ from simulation and theory, the viscosity of a simple molecular fluid could be correlated along an isotherm by selecting an optimal value of V_0 for that molecule at a given temperature. Considering a range of temperatures, the substance-dependent molar core volume V_0 was found to decrease slowly with increasing T . For practical purposes, $V_0(T)$ is usually approximated by a simple polynomial in T [7, 19].

It was found that the hard-sphere model could also be applied successfully to non-spherical molecules by treating them as rough-hard-spheres, for which the expression for viscosity is modified by a simple multiplicative parameter, usually taken to be temperature independent. Thus, a more general expression for the reduced viscosity is

$$\eta^* = (16/5)(2N_A)^{1/3}(\pi / MRT)^{1/2}V_m^{2/3}(\eta / R_\eta). \quad (3)$$

where R_η is called the roughness factor [9]. To correlate the experimental viscosity surface $\eta(T, V_m)$ of a substance, it is therefore necessary to determine the constant R_η and the parameters of $V_0(T)$ that best map the experimental reduced viscosity η^* , defined by Eq. (3), onto the universal function $\eta^*(V^*)$ for smooth hard spheres.

One limitation of the method as originally formulated was that the universal function $\eta^*(V^*)$ for smooth-hard-spheres was subject to significant computational uncertainties at high densities, especially above the equilibrium freezing density. Thus, in later work, $\eta^*(V^*)$ was parameterised by considering the experimental data for normal alkanes; this led to a representation of $\eta^*(V^*)$ by an eight-term polynomial in $(1/V^*)$ valid in the interval $1.5 \leq V^* \leq 5$, corresponding to the normal liquid range of many substances [7]. Recent molecular dynamics calculations for smooth hard spheres provide much improved results [20-22] which we considered further below.

The original hard-sphere scheme for viscosity is successful within its range of applicability, often representing experimental data within $\pm 5\%$. The method was also applied to the thermal conductivity and self-diffusion coefficients for which further universal reference functions are defined [7]. The same molar core-volume function $V_0(T)$ is used for all three properties of a given substance, although different roughness factors apply for viscosity, thermal conductivity and self diffusion. It is important to note that the method is very sensitive to the values of molar volume used, with relative errors in V_m typically leading at high densities to relative errors in η approximately one order of magnitude greater. Thus, when interpreting experimental data at given temperature and pressure, one requires precise knowledge of the corresponding molar volume.

The Extended Hard-Sphere Model

As noted above, the hard-sphere scheme was restricted to reduced volumes in the range $1.5 \leq V^* \leq 5$. Outside this interval, the scheme breaks down; it diverges in the approach to the dilute gas limit, and also exhibits strong deviations with respect to experimental data at high reduced densities. To address the first of these deficiencies, Caudwell [23] proposed the use of an excess reduced viscosity, defined as

$$\Delta\eta^* = \frac{16}{5} (2N_A)^{1/3} \left(\frac{\pi}{MRT} \right)^{1/2} V_m^{2/3} \left(\frac{\eta - \eta_0}{R_\eta} \right), \quad (4)$$

which has the property that $\Delta\eta^* \rightarrow 0$ in the dilute gas limit where $\eta \rightarrow \eta_0$. This ensures that the model behaves reasonably at low densities. Since in the dense fluid region $\eta \gg \eta_0$, the excess reduced viscosity $\Delta\eta^*$ does not differ significantly from η^* and the two are essentially identical at high densities. Thus, Caudwell was able to construct a new universal curve, $\Delta\eta^*(V^*)$, by simply matching it to the original DA correlation for η^* over the range $1.25 \leq V^* \leq 2.5$. No data were fitted in the low-density region $V^* > 2.5$ and the correlation was simply constrained such that $\Delta\eta^* \rightarrow 0$ as $1/V^* \rightarrow \infty$ by means of the following polynomial in reduced density:

$$\log_{10}(1 + \Delta\eta^*) = \sum_{i=1}^7 a_i (1/V^*)^i. \quad (5)$$

In order to address the second deficiency identified above, Ciotta [24] made use of experimental data for alkanes that extend into the high density region $V^* < 1.5$. For each substances and isotherm considered, the data at $V^* \geq 1.5$ were used to determine the reducing parameters R_η and V_0 that best map the experimental reduced viscosities on to the curve proposed by Assael *et al.* [7] The data at smaller reduced volumes were then used to establish the excess reduced viscosity as a function of reduced volume in an extended range spanning

$1.25 \leq V^* \leq 1.5$. Ciotta [24] developed a correlation for $\Delta\eta^*(V^*)$ in the form of Eq. (5) by fitting these new data and by matching to the original scheme in the region $1.5 \leq V^* \leq 2.5$.

The New Reference Function for Reduced Excess Viscosity

In the present work we establish a new reference function for the excess reduced viscosity as defined in Eq. (4). To do this, we consider a large database of critically assessed experimental viscosities for alkanes in gaseous, liquid and supercritical states. The experimental data considered are summarised in Table 1, where we give for each data source the temperature range, the maximum pressure, and the estimated relative uncertainty at 95 % confidence.

For the normal alkanes up to *n*-dodecane, we use in our analysis the correlations proposed by Assael *et al.* [7, 25] for the roughness factor, R_η , and for the molar core volume V_0 . In the case of the roughness factor, the correlation is expressed in terms of carbon number *n* and is [7, 25]

$$R_\eta = 0.995 - 0.0008944n + 0.005427n^2. \quad (6)$$

For the molar core volume, separate correlations, in terms of *T* and *n*, are given for $1 \leq n \leq 4$, $n = 5$ and $6 \leq n \leq 12$ as follows [7, 25]:

for methane to *n*-butane,

$$V_0 / (\text{cm}^3 \cdot \text{mol}^{-1}) = 45.822 - 6.1867\theta^{1/2} + 0.36879\theta - 0.007273 \theta^{3/2} + n(2.17871 \theta^{1/2} - 0.185198\theta + 0.00400369\theta^{3/2}) + n^2(6.95148 - 52.6436\theta^{-1/2}) + n^3(-7.801897 + 42.24493\theta^{-1/2} + 0.4476523\theta^{1/2} - 0.009573512\theta) \quad ; \quad (7)$$

for *n*-pentane,

$$V_0 / (\text{cm}^3 \cdot \text{mol}^{-1}) = 81.1713 - 0.046169\theta; \quad (8)$$

and for *n*-hexane to *n*-dodecane,

$$V_0 / (\text{cm}^3 \cdot \text{mol}^{-1}) = 117.874 + 0.15(-1)^n - 0.25275\theta + 0.000548\theta^2 - 4.246 \times 10^{-7} \theta^3 + (n - 6)(127 - 0.0009\theta)(13.27 + 0.025n), \quad (9)$$

where $\theta = T/K$. The use of Eqs (6) to (9) in our analysis ensures that the new correlation remains compatible with previous correlations of R_η and V_0 . The temperature range considered in our analysis was limited to $110 \leq T/K \leq 400$ to ensure the validity of these correlations.

For the other fluids considered in the determination of $\Delta\eta^*(V^*)$ (i.e. *n*-hexadecane, *n*-octadecane and 2,2,4,4,6,8,8-heptamethylnonane), the values of R_η and $V_0(T)$ were determined as a part of the analysis. The roughness factors were constant for each substance while $V_0(T)$ was represented by a quadratic polynomial of the form:

$$V_0 / (\text{cm}^3 \cdot \text{mol}^{-1}) = c_0 + c_1\theta + c_2\theta^2. \quad (10)$$

Table 1. Summary of selected literature data for the viscosity of alkanes.^a

Substance	Source	$T_{\min}/K$	$T_{\max}/K$	$p_{\max}/MPa$	$10^2 U_r$	$(1/V^*)_{\max}$	$10^2 \Delta_{AAD}$	
Methane	Baron <i>et al.</i> [26]	325	408	55	1.0	0.29	2.0	<i>b</i>
	Carmichael <i>et al.</i> [27]	277	478	35	0.5	0.29	1.9	<i>b</i>
	Chuang <i>et al.</i> [28]	173	273	50	0.5	0.49	3.8	<i>b</i>
	Diller [29]	100	300	32	1.0	0.59	3.4	<i>b</i>
	Giddings <i>et al.</i> [30]	283	411	55	0.5	0.34	2.5	<i>b</i>
	Hellemans <i>et al.</i> [31]	97	146	10	2.0	0.58	1.5	<i>b</i>
	Huang <i>et al.</i> [32]	153	273	35	1.2	0.51	3.4	<i>b</i>
	Kestin and Yata [33]	293	303	2.6	0.05	0.02	0.7	<i>b</i>
	Knapstad [34]	293	423	40		0.28	2.6	<i>b</i>
	Ross and Brown [35]	223	298	69	1.0	0.43	3.2	<i>b</i>
	Van der Gulik <i>et al.</i> [36],[37]	273	298	1000	0.5	0.64	3.6	<i>b</i>
Ethane	Baron <i>et al.</i> [26]	325	408	55	1.0	0.44	2.7	<i>b</i>
	Carmichael and Sage [38]	300	478	36	0.5	0.44	2.0	<i>b</i>
	Diller and Saber [39]	100	290	31	2.0	0.73	2.8	<i>b</i>
	Eakin and Starling [40]	311	444	55		0.46	1.7	<i>b</i>
	Iwasaki and Takahashi [41]	298	348	13	0.3	0.28	2.2	<i>b</i>
	Swift <i>et al.</i> [42]	193	305	5	2.1	0.56	1.7	<i>b</i>
<i>n</i> -Propane	Baron <i>et al.</i> [26]	325	408	55	1.0	0.53	2.3	<i>b</i>
	Carmichael <i>et al.</i> [43]	278	478	35	0.5	0.56	0.7	<i>b</i>
	Diller [44]	90	300	31	2.0	0.79	2.1	<i>b</i>
	Giddings <i>et al.</i> [30]	278	378	55	0.5	0.57	1.0	<i>b</i>
	Huang <i>et al.</i> [32]	173	273	34	1.2	0.53	1.9	<i>b</i>
	Starling <i>et al.</i> [45]	311	411	55	0.5	0.54	1.1	<i>b</i>
	Wilhelm and Vogel [46]·[47]	298	423	20	0.33	0.41	1.6	<i>c</i>
<i>n</i> -Butane	Abe <i>et al.</i> [48]	298	468	0.1	0.2	0.002	0.3	<i>b</i>
	Carmichael and Sage [49]	278	478	35	0.5	0.61	0.9	<i>b</i>
	Diller and van Poolen [50]	140	300	32	1.0	0.77	2.4	<i>b</i>
	Dolan <i>et al.</i> [51]	311	444	55	0.5	0.59	1.7	<i>b</i>
	Kestin and Yata [33]	293	303	0.17	0.05	0.005	0.8	<i>b</i>
	Swift <i>et al.</i> [42]	293	373	1.7	2.4	0.55	1.6	<i>b</i>
<i>n</i> -Pentane	Audonnet and Padua [52]	303	383	100	2.5	0.65	1.9	<i>c</i>
	Oliveira and Wakeham [53]	303	323	251	0.5	0.70	1.7	<i>c</i>
	Collings and McLaughlin [54]	303	323	588		0.64	3.7	<i>d</i>
	Brazier and Feeeman [55]	303	303	400		0.65	3.2	<i>d</i>
<i>n</i> -Hexane	Dymond <i>et al.</i> [56]	298	373	420	2.0	0.75	1.8	<i>c</i>
	Oliveira and Wakeham [53]	303	348	251	0.5	0.72	2.8	<i>d</i>
	Isdale <i>et al.</i> [57]	298	373	500	2.0	0.68	2.9	<i>d</i>
	Brazier and Feeeman [55]	303	303	400		0.70	3.0	<i>d</i>
<i>n</i> -Heptane	Assael and Papadaki [58]	303	323	69	0.5	0.68	0.5	<i>c</i>
	Assael <i>et al.</i> [59]	303	348	249	0.5	0.69	0.9	<i>d</i>
	Assael <i>et al.</i> [60]	303	343	100	0.5	0.69	0.8	<i>d, e</i>
	Zeberg-Mikkelsen [61]	293	353	100	2.0	0.70	1.6	<i>b</i>

Substance	Source	$T_{\min}/\text{K}$	$T_{\max}/\text{K}$	$p_{\max}/\text{MPa}$	$10^2 U_r$	$(1/V^*)_{\max}$	$10^2 \Delta_{\text{AAD}}$	
<i>n</i> -Octane	Caudwell <i>et al.</i> [62]	298	473	200	2.0	0.75	1.7	<i>c</i>
	Harris <i>et al.</i> [63]	298	353	373	2.0	0.80	2.9	<i>c</i>
	Dymond <i>et al.</i> [64]	298	373	506	2.0	0.75	2.2	<i>e</i>
	Tanaka <i>et al.</i> [65]	298	348	151	2.0	0.73	1.9	<i>c</i>
	Oliveira and Wakeham [53]	303	348	253	0.5	0.75	1.7	<i>c</i>
<i>n</i> -Nonane	Assael and Papadaki [58]	303	323	69	0.5	0.71	1.4	<i>c</i>
<i>n</i> -Decane	Caudwell <i>et al.</i> [62]	298	373	200	2.0	0.77	1.9	<i>c</i>
	Oliveira and Wakeham [53]	303	348	253	0.5	0.77	1.7	<i>e</i>
	Assael <i>et al.</i> [66]	303	323	64	0.5	0.72	1.8	<i>e</i>
	Carmichael <i>et al.</i> [67]	310	377	36		0.70	1.1	<i>e</i>
	Audonnet and Padua [68]	298	393	75	3.0	0.72	1.8	<i>c</i>
<i>n</i> -Undecane	Assael and Papadaki [58]	303	323	62	0.5	0.73	0.6	<i>c</i>
<i>n</i> -Dodecane	Caudwell <i>et al.</i> [62]	298	473	200	2.0	0.78	2.6	<i>c</i>
	Tanaka <i>et al.</i> [65]	298	348	150	2.0	0.76	2.3	<i>e</i>
	Dymond <i>et al.</i> [64]	298	373	502	0.5	0.77	2.9	<i>e</i>
<i>n</i> -Hexadecane	Ciotto [24]	298	473	102	2.0	0.77	0.8	<i>c</i>
	Dymond <i>et al.</i> [56]	298	373	425	0.5	0.77	1.1	<i>f</i>
	Tanaka <i>et al.</i> [65]	298	348	151	2.0	0.77	0.8	<i>f</i>
	Rajagopal <i>et al.</i> [69]	318	413	62	2.4	0.76	1.7	<i>f</i>
<i>n</i> -Octadecane	Caudwell <i>et al.</i> [70]	323	473	91	2.0	0.78	0.9	<i>c</i>
	Hogenboom <i>et al.</i> [71]	333	408	360		0.76	1.8	<i>g</i>
HMN ^{<i>h</i>}	Ijaz [72]	298	448	135	2.0	0.84	2.5	<i>c</i>
	Zeberg-Mikkelsen <i>et al.</i> [73]	293	353	100	2.0	0.83	2.0	<i>c</i>
	Canet <i>et al.</i> [74]	293	353	100	1.0	0.83	2.6	<i>c</i>

^a $T_{\min}$, $T_{\max}$, and $p_{\max}$ are the minimum and maximum temperature and the maximum pressure, respectively, of the published data set; U_r is the expanded relative uncertainty of the viscosity at 95% confidence as specified in, or estimated from, the publication; $(1/V^*)_{\max}$ is the maximum reduced density of the data after truncation of the temperature and pressure ranges; Δ_{AAD} is the absolute average relative deviation of the dataset from the present correlation.

^b Density calculated from REFPROP [75].

^c Density given by the authors.

^d Density calculated from REFPROP [75] and analysis limited to $p \leq 105$ MPa.

^e Density calculated from model of Caudwell *et al.* [62] and analysis limited to $p \leq 210$ MPa.

^f Density calculated from the model of Ciotto [24] and analysis limited to $p \leq 105$ MPa.

^g Density calculated from model of Caudwell *et al.* [62] and analysis limited to $p \leq 105$ MPa.

^h 2,2,4,4,6,8,8-heptamethylnonane.

Since the method is very sensitive to the values of density used, careful attention was paid to this point. The method followed to obtain the molar density is indicated in Table 1 for each dataset. In some cases, the choice of density model necessitated the exclusion of viscosity data at pressures beyond the specified limits for that model, although extrapolation by up to 5% of the maximum pressure was allowed to prevent exclusion of points only just above the nominal maximum pressure for the selected density model. For the light alkanes up to *n*-butane [76-79], densities were calculated from reference-quality equations of state (EoS) available in the REFPROP database [75]; exceptionally, the isochoric data of Wilhelm *et al.* [46, 47] for propane were analysed with the densities reported by the authors. For *n*-pentane to *n*-dodecane one of three methods was selected for each dataset as follows: (i) densities specified by the authors; (ii) the EoS of Span and Wagner [80]; (iii) the correlations of Caudwell *et al.* [62, 70]. For *n*-hexadecane, the correlation of Ciotta [24] was used; for *n*-octadecane, the correlation of Caudwell *et al.* [70] was used; and for 2,2,4,4,6,8,8-heptamethylnonane, we used the densities reported by the authors.

The dilute-gas viscosity $\eta_0(T)$ was also required for each substance. For methane to *n*-octane, this was taken from the correlations available in the REFPROP database [75]. For the other substances, η_0 was actually negligible compared with the experimental viscosities considered but, for sake of completeness, Vicharelli's [81] analytical approximation for the Lennard-Jones (12,6) potential was used with parameters estimated from the critical temperature and pressure [82].

Following restriction of the dataset to temperatures between 110 K and 400 K and to pressures at which reliable densities were available, approximately 2700 data points remained covering the 15 substances at reduced densities ($1/V^*$) up to approximately 0.84. For methane to *n*-dodecane, Eqs (6) to (9) apply for V_0 and R_η allowing $\Delta\eta^*$ to be computed from the experimental data (supplemented, where noted in Table 1, by a model for the density). The results are plotted in Figure 1 over the entire range of reduced densities considered ($1/V^* \leq 0.8$). At high densities, the data fall onto a single curve irrespective of temperature and substance. Also shown in Figure 1 are the molecular dynamics results of Sigurgeirsson and Heyes [20] for dense hard spheres; these are seen to be in fair agreement with the universal curve determined from experimental data. The experimental data at reduced densities below 0.5, show some dispersion but nevertheless also conform approximately to a universal curve. The term $V_m^{2/3}$ in Eq. (4) has the effect of amplifying small experimental errors as $1/V^* \rightarrow 0$ and is responsible for the deviations from a universal curve seen near the origin in Figure 1(a).

Initial values for the roughness factor and the molar core volume at each temperature for *n*-hexadecane, *n*-octadecane and 2,2,4,4,6,8,8-heptamethylnonane were determined by matching the data for these substances to the universal curve defined by the other alkane data ($n \leq 12$ and $1/V^* \leq 0.8$). Applying the values of the roughness factor and the molar core volume to the viscosity data at higher densities, then permitted the universal curve to be extended up to $1/V^* = 0.84$, as shown in Figure 1(b). Initial estimates of the parameters a_i in Eq. (5), and also of c_i in eq. (10), were obtained as a starting point for the subsequent non-linear optimisation by fitting the results of this analysis.

The final parameters a_i in Eq. (5) for the new universal curve $\Delta\eta^*$ were determined so as to minimise a weighted objective function χ^2 defined as follows:

$$\chi^2 = \sum_{i=1}^{15} \left[(1/N_i) \sum_{j=1}^{N_i} \{ (\eta_{i,j,\text{exp}} - \eta_{i,j,\text{calc}}) / \eta_{i,j,\text{exp}} \}^2 \right]. \quad (11)$$

Here, $\eta_{i,j,\text{exp}}$ is the j^{th} experimental datum for substance i , $\eta_{i,j,\text{calc}}$ is the corresponding value calculated from the model, and N_i is the number of data points considered for substance i . This objective function places equal weight on each substance and is designed to achieve the best possible fit to the raw viscosity data. In the process, the parameters R_η and c_i ($i = 1$ to 3) were also adjusted for n -hexadecane, n -octadecane and 2,2,4,4,6,8,8-heptamethylnonane. The parameters so determined are given in Tables 2 and 3.

Table 2. Parameter in Eq. (5) for the universal curve.

i	1	2	3	4	5	6	7
a_i	6.26871	-48.4793	243.447	-653.257	974.312	-763.616	251.193

Table 3. Roughness factors R_η and parameters c_i in the correlation of the molar core volume.

Substance	R_η	c_1	c_2	c_3
<i>n</i> -Hexadecane	2.008	2.9228×10^2	-3.3615×10^{-1}	3.1128×10^{-4}
HMN	1.060	2.7126×10^2	-2.1219×10^{-1}	1.9798×10^{-4}
Octadecane	2.232	2.8364×10^2	-1.2633×10^{-1}	0
DIDP	2.333	5.8329×10^2	-9.0877×10^{-1}	9.1493×10^{-4}
DEHP	3.077	5.4565×10^2	-1.0936×10^0	1.2590×10^{-3}

Table 4. Goodness of fit statistics for the determination of the universal curve.

Substance	$10^2 \Delta_{\text{AAD}}$	$10^2 \Delta_{\text{MAD}}$	$10^2 \Delta_{\text{bias}}$
Methane	2.9	11.8	-1.8
Ethane	2.3	9.6	1.7
<i>n</i> -Propane	1.4	6.3	0.3
<i>n</i> -Butane	1.7	7.5	1.0
<i>n</i> -Pentane	1.9	7.7	0.6
<i>n</i> -Hexane	2.5	5.3	1.0
<i>n</i> -Heptane	0.9	2.9	0.3
<i>n</i> -Octane	2.1	8.0	-1.6
<i>n</i> -Nonane	1.4	2.5	-1.4
<i>n</i> -Decane	1.7	4.5	-0.5
<i>n</i> -Undecane	0.6	1.8	-0.2
<i>n</i> -Dodecane	2.6	8.5	1.1
<i>n</i> -Hexadecane	1.2	3.9	0.0
2,2,4,4,6,8,8-Heptamethylnonane	2.4	9.7	0.1
<i>n</i> -Octadecane	1.1	3.8	0.0
DIDP	1.3	5.6	0.0
DEHP	4.8	11.7	0.3

Comparison with Experimental Data

Table 4 details the goodness of fit on a substance-by-substance basis in terms of the average absolute relative deviation Δ_{AAD} , the maximum absolute relative deviation Δ_{MAD} , and the average relative deviation, or bias, Δ_{bias} . We also give in Table 1 the average absolute relative deviation for each individual dataset from the present correlation; these figures may be compared with the estimated relative uncertainties U_r , given in the same table, which mostly fall between (0.5 and 2.0) %. The performance of the model in comparison with the data used in the determination of the new reference function is illustrated in Figures 2 to 4. Figure 2 shows the data for methane to *n*-butane. For methane, the extended hard-sphere model performs slightly less well than the original scheme at intermediate reduced densities, with significant negative deviations for reduced densities $1/V^*$ between 0.3 and 0.5, but at higher densities, the model performs as well as the original (for comparison, the original scheme correlates the data at $1/V^* \geq 0.2$, with $\Delta_{AAD} = 2.6$ % and $\Delta_{MAD} = 8.7$ %). It is notable that the data for van der Gulik [36] at $T = 298.15$ K, which extends up to $p = 1000$ MPa, are represented with relative deviations of between +3% and -6%, whereas van der Gulik's [37] data at $T = 273$ K show generally larger deviations of between +2% and -12%. The deviations for ethane, seen in Figure 2(b), also show some dependence on $1/V^*$ but are generally satisfactory at all densities. For propane and butane, the deviations are mostly within $\pm 5\%$ with less evidence of systematic behaviour. Figure 3 shows the results for *n*-pentane to *n*-octane. These cover the range $0.5 \leq 1/V^* \leq 0.8$ and the vast majority of these data fall within $\pm 5\%$. The deviations for *n*-heptane are especially small with $\Delta_{AAD} < 1$ %. Figures 4(a) and 4(b), for *n*-nonane to *n*-dodecane, show the remaining data covered by the V_0 correlation of Assael *et al.* [7] and again the deviations are mostly within $\pm 5\%$. Figures 4(c) and 4(d) show that the data for *n*-hexadecane, *n*-octadecane and the hexadecane isomer 2,2,4,4,6,8,8-heptamethylnonane are all represented by the correlation in a satisfactory way. Overall, more than 97% of the 2700 viscosity data points fall within $\pm 5\%$ of the correlation and the maximum absolute relative deviation is 12%.

As a further test of the new universal curve in the region of high reduced density, we consider the available high-pressure experimental viscosity data for diisodecyl phthalate (DIDP) [83-85] and bis(2-ethylhexyl) phthalate (DEHP) [85], which together span a range of viscosities from approximately 5 mPa·s to 2500 mPa·s. For these two substances, we made the approximation $\eta_0 \approx 0$. For DIDP, all densities were calculated from the equation of state of Peleties *et al.* [86]. In the case of DEHP, the densities were those reported by the author based on measurements at $p = 0.1$ MPa and literature data for the compressibility of the liquid. It is notable that the data for DEHP cover reduced densities up to $1/V^* = 0.90$. The parameters R_η and c_i ($i = 1$ to 3) were optimised for each of these liquids in a fit to the extended hard-sphere model and the results are given in Tables 3 and 4. For DIDP, the data from the three different sources considered are represented remarkably well with relative deviations mostly within $\pm 5\%$. In contrast, deviation spanning $\pm 40\%$ are found when the original hard-sphere scheme was applied to these data. The viscosity deviations found for DEHP are larger but mostly within $\pm 10\%$, whereas deviations spanning $\pm 75\%$ were found with the original hard-sphere scheme. Thus, the present model is seen to be a marked improvement for high-viscosity liquids.

Conclusion

The extended hard-sphere model developed in this work significantly improves the performance of the DA method at high densities, allowing data to be correlated at reduced densities up to approximately 0.9. The method also behaves reasonably in the approach to zero density and thus the approximation is valid over almost the entire fluid range. The extended hard-sphere model does require more information, namely the values of zero-density viscosity for a given temperature. For highly viscous fluids this term can be neglected, while for other fluids correlations or estimation methods are available in literature.

The proposed model retains the correlations of V_0 and R_η developed in earlier work for n-alkanes smaller than tridecane. As with the original DA approach, the method developed here is very sensitive to density and an accurate equation of state is needed if density is to be determined from specified values of temperature and pressure. We suggest that a similar methodology could be developed for thermal conductivity and self diffusion. As in the development of the original DA scheme, simultaneous analysis of viscosity, thermal conductivity and self diffusion may be advantageous in terms of obtaining extended universal curves that permit all three properties to be correlated with the same molar core volume function, $V_0(T)$, for a given substances.

Acknowledgement: this work was supported in part by a grant from the Engineering and Physical Sciences Research Council (grant reference EP/E007031).

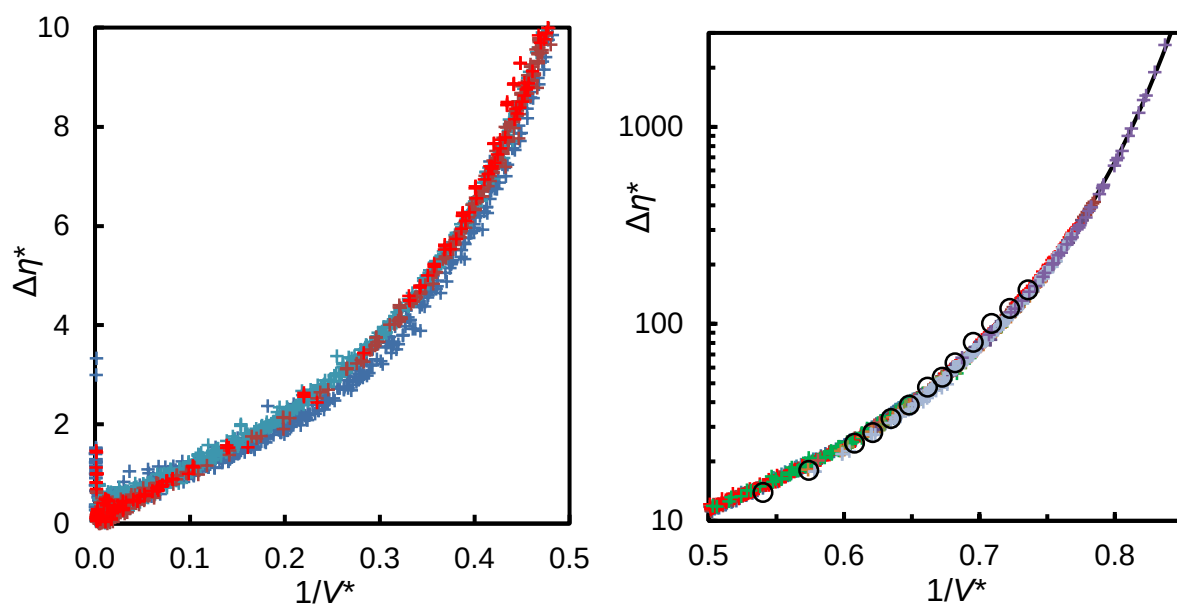


Figure 1 (color online). Reduced excess viscosities $\Delta\eta^*$ determined from the experimental data from the alkanes listed in Table 1 (crosses) and from molecular simulation (circles).

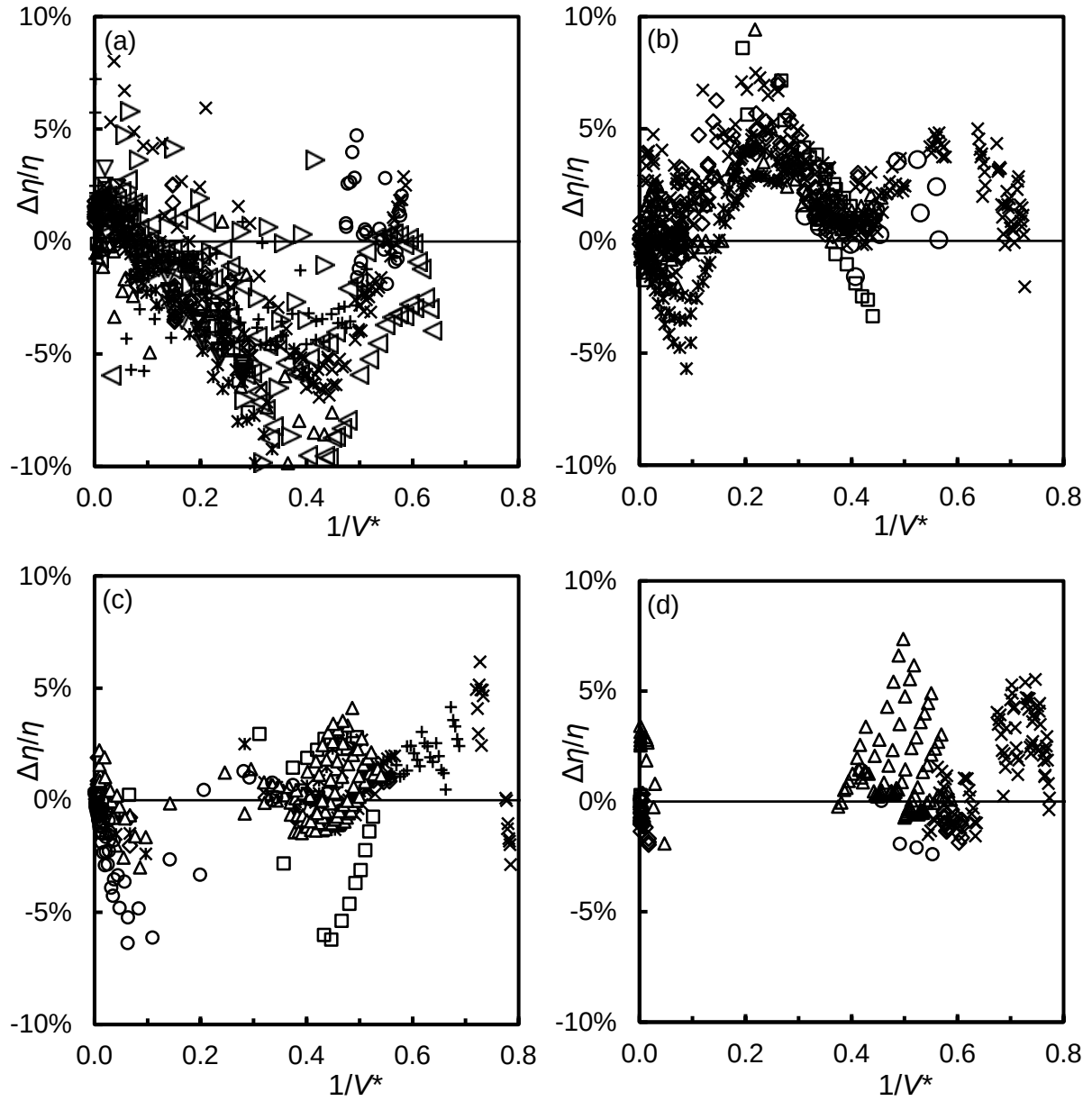


Figure 2. Deviations $\Delta\eta$ of experimental viscosity data from the extended hard-sphere model. (a) Methane: $\square$ [26]; $\diamond$ [27]; $\triangle$ [28]; $\times$ [29]; $*$ [30]; $\circ$ [31]; $+$ [32]; $—$ [33]; ∇ [34]; $\triangleright$ [35]; $\triangleleft$ [36, 37]. (b) Ethane: $\square$ [26]; $\diamond$ [38]; $\times$ [39]; $\triangle$ [40]; $*$ [41]; $\circ$ [42]. (c) *n*-Propane: $\square$ [26]; $\diamond$ [43]; $\times$ [44]; $*$ [30]; $+$ [32]; $\triangle$ [45]; $\circ$ [46, 47]. (d) *n*-Butane: $\square$ [48]; $\diamond$ [49]; $\times$ [50]; $\triangle$ [51]; $—$ [33]; $\circ$ [42].

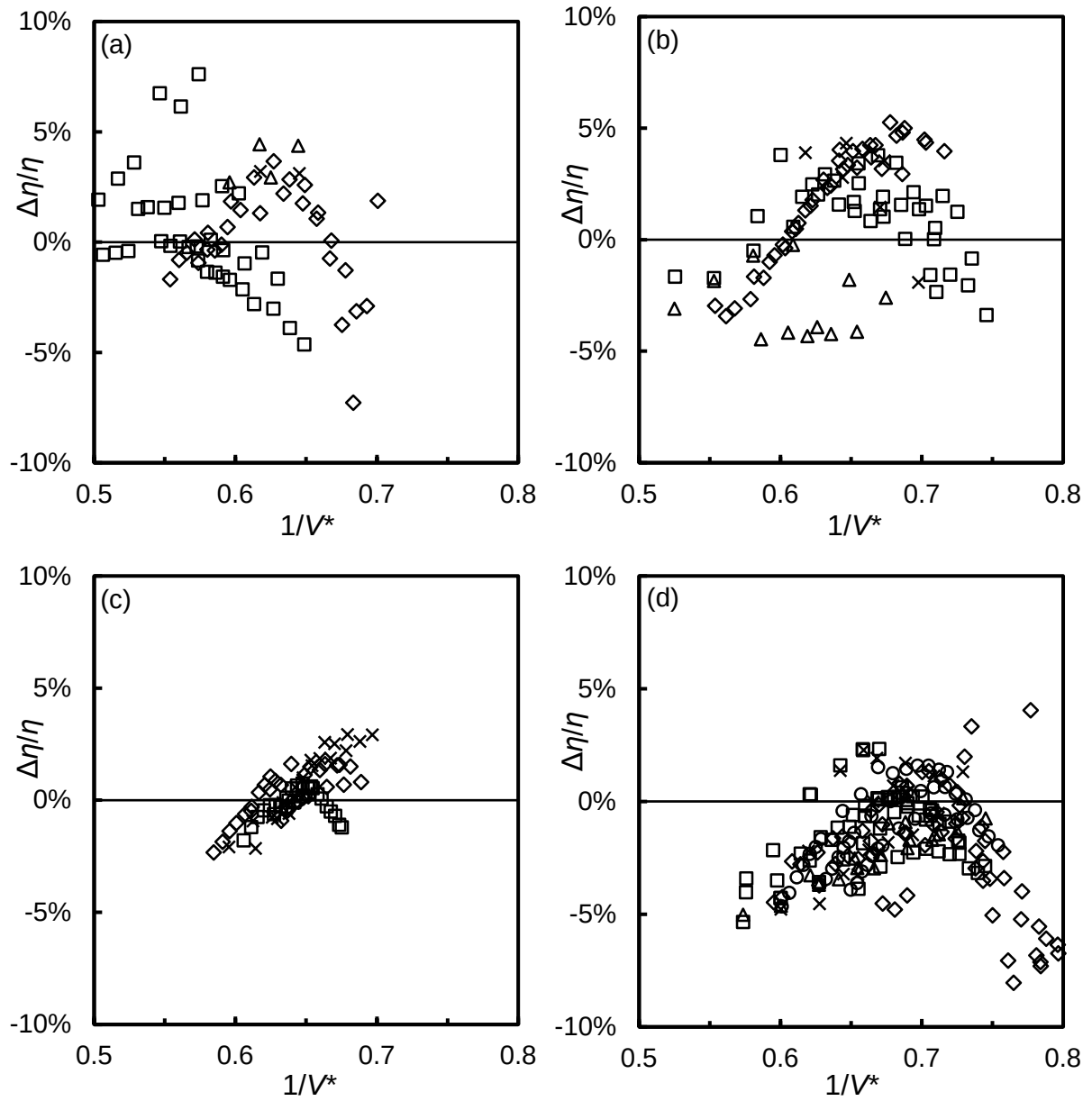


Figure 3. Deviations $\Delta\eta$ of experimental viscosity data from the extended hard-sphere model. (a) *n*-Pentane: $\square$ [52]; $\diamond$ [53]; $\triangle$ [54]; $\times$ [55]. (b) *n*-Hexane: $\square$ [56]; $\diamond$ [53]; $\triangle$ [57]; $\times$ [55]. (c) *n*-Heptane: $\square$ [58]; $\diamond$ [59]; $\triangle$ [60]; $\times$ [61]. (d) *n*-Octane: $\square$ [62]; $\diamond$ [63]; $\triangle$ [64]; $\times$ [65]; $\circ$ [53].

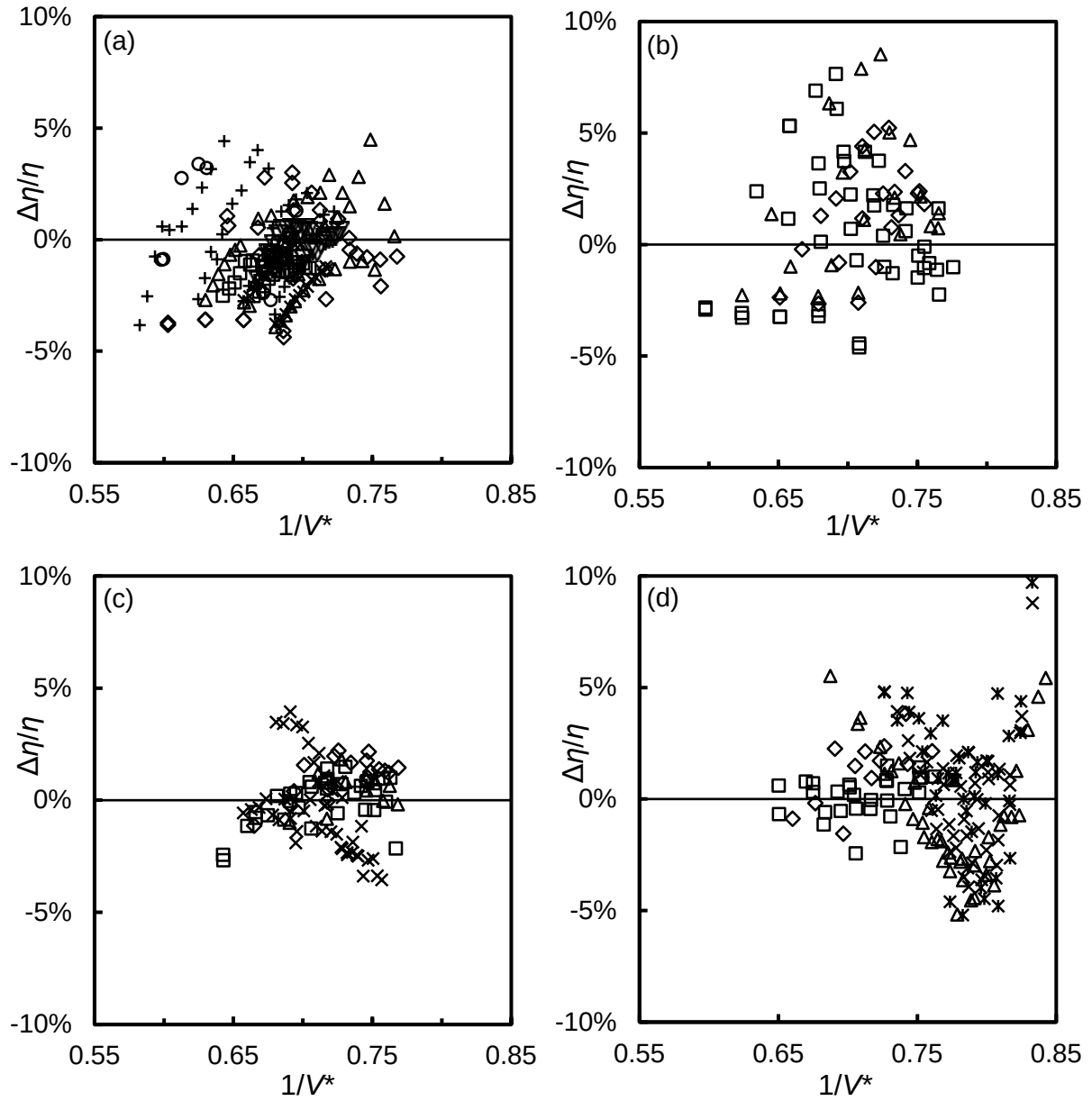


Figure 4. Deviations $\Delta\eta$ of experimental viscosity data from the extended hard-sphere model. (a) *n*-Nonane, *n*-decane and *n*-undecane: $\square$ [58]; $\diamond$ [62]; $\triangle$ [53]; $\times$ [66]; $\circ$ [67]; $+$ [68]; ∇ [58]. (b) *n*-Dodecane: $\square$ [70]; $\diamond$ [65]; $\triangle$ [64]. (c) *n*-Hexadecane: $\square$ [24]; $\diamond$ [56]; $\triangle$ [65]; $\times$ [69]. (d) *n*-Octadecane and 2,2,4,4,6,8,8-hexamethylnonane: $\square$ [70]; $\diamond$ [71]; $\triangle$ [72]; $\times$ [73]; $*$ [74].

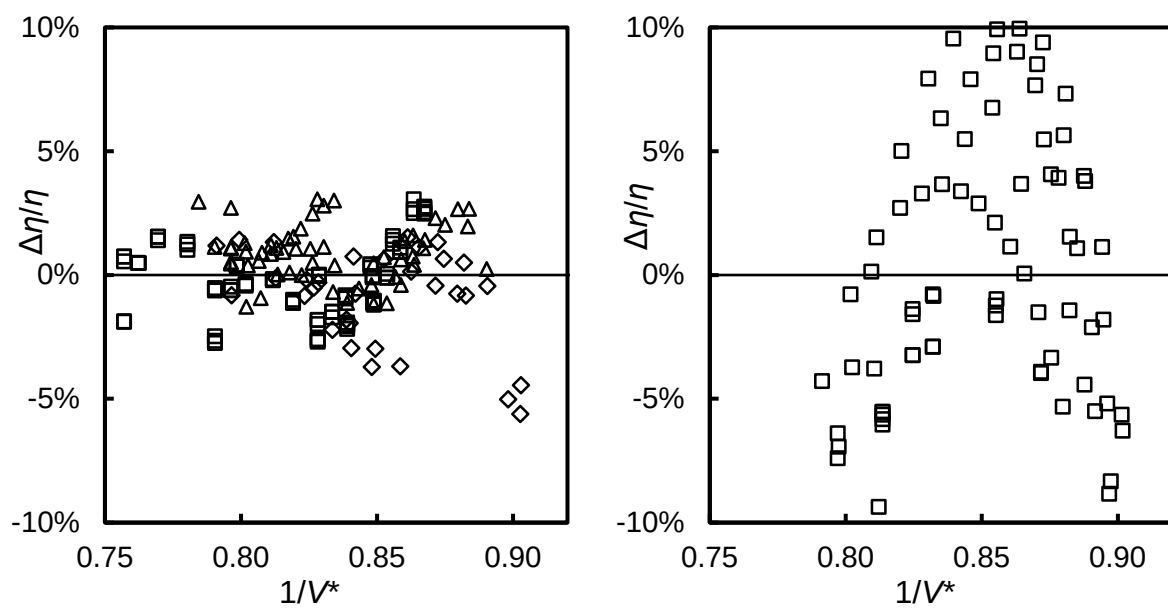


Figure 5. Deviations $\Delta\eta$ of experimental viscosity data from the extended hard-sphere model. (a) DIDP: □[83]; ◇[84]; △[84]. (b) DEHP: □[85].

References

- [1] F.R.W. McCourt, J.J.M. Beenakker, W.E. Köhler, I. Kučšer, Nonequilibrium Phenomena in Polyatomic Gases, Clarendon Press, Oxford, 1990.
- [2] S. Bock, E. Bich, E. Vogel, A.S. Dickinson, V. Vesovic, Calculation of the transport properties of carbon dioxide. I. Shear viscosity, viscomagnetic effects, and self-diffusion, *J. Chem. Phys.*, 117 (2002) 2151-2160.
- [3] R. Hellmann, E. Bich, E. Vogel, A.S. Dickinson, V. Vesovic, Calculation of the transport and relaxation properties of methane. I. Shear viscosity, viscomagnetic effects, and self-diffusion, *J. Chem. Phys.*, 129 (2008).
- [4] R. Hellmann, E. Bich, E. Vogel, A.S. Dickinson, V. Vesovic, Calculation of the transport and relaxation properties of dilute water vapor, *J. Chem. Phys.*, 131 (2009).
- [5] R. Hellmann, E. Bich, E. Vogel, V. Vesovic, Ab initio intermolecular potential energy surface and thermophysical properties of hydrogen sulfide, *PCCP*, 13 (2011) 13749-13758.
- [6] R. Hellmann, Ab initio potential energy surface for the nitrogen molecule pair and thermophysical properties of nitrogen gas, *Mol. Phys.*, 111 (2013) 387-401.
- [7] M.J. Assael, J.H. Dymond, M. Papadaki, P.M. Patterson, Correlation and Prediction of Dense Fluid Transport-Coefficients .1. Normal-Alkanes, *Int. J. Thermophys.*, 13 (1992) 269-281.
- [8] M.J. Assael, J.H. Dymond, M. Papadaki, P.M. Patterson, Correlation and Prediction of Dense Fluid Transport-Coefficients .2. Simple Molecular Fluids, *Fluid Phase Equilib.*, 75 (1992) 245-255.
- [9] M.J. Assael, J.H. Dymond, M. Papadaki, P.M. Patterson, Correlation and Prediction of Dense Fluid Transport-Coefficients .3. Normal-Alkane Mixtures, *Int. J. Thermophys.*, 13 (1992) 659-669.
- [10] M.J. Assael, J.H. Dymond, P.M. Patterson, Correlation and Prediction of Dense Fluid Transport-Coefficients .4. A Note on Diffusion, *Int. J. Thermophys.*, 13 (1992) 729-733.
- [11] M.J. Assael, J.H. Dymond, P.M. Patterson, Correlation and Prediction of Dense Fluid Transport-Coefficients .5. Aromatic-Hydrocarbons, *Int. J. Thermophys.*, 13 (1992) 895-905.
- [12] V. Vesovic, W.A. Wakeham, The Prediction of the Viscosity of Dense Gas-Mixtures, *Int. J. Thermophys.*, 10 (1989) 125-132.
- [13] V. Vesovic, W.A. Wakeham, Prediction of the Viscosity of Fluid Mixtures over Wide Ranges of Temperature and Pressure, *Chem. Eng. Sci.*, 44 (1989) 2181-2189.
- [14] D.D. Royal, V. Vesovic, J.P.M. Trusler, W.A. Wakeham, Prediction of the viscosity of dense fluid mixtures, *Mol. Phys.*, 101 (2003) 339-352.
- [15] A.S. de Wijn, V. Vesovic, G. Jackson, J.P.M. Trusler, A kinetic theory description of the viscosity of dense fluids consisting of chain molecules, *J. Chem. Phys.*, 128 (2008).
- [16] A.S. de Wijn, N. Riesco, G. Jackson, J.P.M. Trusler, V. Vesovic, Viscosity of liquid mixtures: The Vesovic-Wakeham method for chain molecules, *J. Chem. Phys.*, 136 (2012).
- [17] J.H. Dymond, Transport Properties of Dense Fluids, in: P.E. Liley (Ed.) Sixth Symposium on Thermophysical Properties, The American Society of Mechanical Engineers, Atlanta, Georgia, U.S.A., 1973, pp. 143-157.
- [18] J.H. Dymond, Interpretation of transport-coefficients on basis of Van der Waals model.1. Dense fluids, *Physica*, 75 (1974) 100-114.
- [19] J. Millat, J.H. Dymond, C.A. Nieto de Castro, Transport properties of fluids : their correlation, prediction, and estimation, Cambridge University Press, New York, 1996.
- [20] H. Sigurgeirsson, D.M. Heyes, Transport coefficients of hard sphere fluids, *Mol. Phys.*, 101 (2003) 469-482.
- [21] D.M. Heyes, A.C. Branka, Transport coefficients of soft repulsive particle fluids, *J Phys-Condens Mat*, 20 (2008).
- [22] D.M. Heyes, A.C. Branka, Self-diffusion coefficients and shear viscosity of inverse power fluids: from hard- to soft-spheres, *PCCP*, 10 (2008) 4036-4044.
- [23] D.R. Cudwell, Viscosity of Dense Fluid Mixtures, PhD Thesis, University of London, 2004.
- [24] F. Ciotta, Viscosity of Asymmetric Liquid Mixtures under Extreme Conditions, PhD Thesis, Imperial College London, 2010.
- [25] M.J. Assael, J.P.M. Trusler, T.F. Tsolakis, Thermophysical Properties of Fluids, Imperial College Press, 1996.

- [26] J.D. Baron, J.G. Roof, F.W. Wells, Viscosity of Nitrogen, Methane, Ethane and Propane at Elevated Temperature and Pressure, *J. Chem. Eng. Data*, 4 (1959) 283-288.
- [27] L.T. Carmichael, V.M. Berry, B.H. Sage, Viscosity of Hydrocarbons. Methane, *J. Chem. Eng. Data*, 10 (1965) 57-61.
- [28] S.Y. Chuang, P.S. Chapple, R. Kobayashi, Viscosity of Methane, Hydrogen, and 4 Mixtures of Methane and Hydrogen from -100°C to 0°C at High-Pressures, *J. Chem. Eng. Data*, 21 (1976) 403-411.
- [29] D.E. Diller, Measurements of the Viscosity of Compressed Gaseous and Liquid Methane, *Physica A*, 104 (1980) 417-426.
- [30] J.G. Giddings, J.T.F. Kao, R. Kobayashi, Development of a High-Pressure Capillary-Tube Viscometer and its Application to Methane, Propane and Their Mixtures in the Gaseous and Liquid Regions, *J. Chem. Phys.*, 45 (1966) 578-586.
- [31] J. Hellemans, H. Zink, O. Van Paemel, The Viscosity of Liquid Argon and Liquid Methane along Isotherms as a Function of Pressure, *Physica*, 46 (1970) 395-410.
- [32] E.T.S. Huang, G.W. Swift, F. Kurata, Viscosities of Methane and Propane at Low Temperatures and High Pressures, *AIChE J.*, 12 (1966) 932-936.
- [33] J. Kestin, J. Yata, Viscosity and Diffusion Coefficient of Six Binary Mixtures, *J. Chem. Phys.*, 49 (1968) 4780-4791.
- [34] B. Knapstad, Viscosity of n-Decane - Methane at Elevated Temperature and Pressure, PhD Thesis, Universitetet i Trondheim, 1986.
- [35] J.F. Ross, G.M. Brown, Viscosities of Gases at High Pressures, *Ind. Eng. Chem.*, 49 (1957) 2026-2033.
- [36] P.S. van der Gulik, R. Mostert, H.R. Vandenberg, The Viscosity of Methane at 25 °C up to 10 Kbar, *Physica A*, 151 (1988) 153-166.
- [37] P.S. van der Gulik, R. Mostert, H.R. Vandenberg, The Viscosity of Methane at 273 K up to 1 GPa, *Fluid Phase Equilib.*, 79 (1992) 301-311.
- [38] L.T. Carmichael, B.H. Sage, Measurements of the Viscosity of Compressed Gaseous and Liquid Ethane, *Physica A*, 108 (1963) 143-152.
- [39] D.E. Diller, J.M. Saber, Measurements of the Viscosity of Compressed Gaseous and Liquid Ethane, *Physica A*, 108 (1981) 143-152.
- [40] B.E. Eakin, K.E. Starling, Liquid, Gas and Dense Fluid Viscosity of Ethane, *J. Chem. Eng. Data*, 7 (1962) 33-36.
- [41] H. Iwasaki, M. Takahashi, Viscosity of Carbon-Dioxide and Ethane, *J. Chem. Phys.*, 74 (1981) 1930-1943.
- [42] G.W. Swift, J. Lohrenz, F. Kurata, Liquid Viscosities Above the Normal Boiling Point for Methane, Ethane, Propane and n-Butane, *AIChE J.*, 6 (1960) 415-419.
- [43] L.T. Carmichael, V.M. Berry, B.H. Sage, Viscosity of Hydrocarbons. Propane, *J. Chem. Eng. Data*, 9 (1964) 411-415.
- [44] D.E. Diller, Measurements of the Viscosity of Saturated and Compressed Liquid Propane, *J. Chem. Eng. Data*, 27 (1982) 240-243.
- [45] K.E. Starling, B.E. Eakin, R.T. Ellington, Liquid, Gas and Dense-Fluid Viscosity of Propane, *AIChE J.*, 6 (1960) 438-442.
- [46] J. Wilhelm, E. Vogel, Viscosity Measurements on Gaseous Argon, Krypton, and Propane, *Int. J. Thermophys.*, 21 (2000) 301-318.
- [47] J. Wilhelm, E. Vogel, Viscosity Measurements on Gaseous Propane: Re-evaluation (vol 46, pg 1467, 2001), *J. Chem. Eng. Data*, 56 (2011) 1722-1729.
- [48] Y. Abe, J. Kestin, H.E. Khalifa, W.A. Wakeham, Viscosity of Normal Butane, Isobutane and Their Mixtures, *Physica A*, 97 (1979) 296-305.
- [49] L.T. Carmichael, B.H. Sage, Viscosity of Hydrocarbons. n-Butane, *J. Chem. Eng. Data*, 8 (1963) 612-616.
- [50] D.E. Diller, L.J. Vanpoolen, Measurements of the Viscosities of Saturated and Compressed Liquid Normal Butane and Isobutane, *Int. J. Thermophys.*, 6 (1985) 43-62.
- [51] J.P. Dolan, K.E. Starling, A.L. Lee, B.E. Eakin, R.T. Ellington, Liquid, Gas and Dense Fluid Viscosity of n-Butane, *J. Chem. Eng. Data*, 8 (1963) 396-399.
- [52] F. Audonnet, A.A.H. Padua, Simultaneous measurement of density and viscosity of n-pentane from 298 to 383 K and up to 100 MPa using a vibrating-wire instrument, *Fluid Phase Equilib.*, 181 (2001) 147-161.

- [53] C.M.B.P. Oliveira, W.A. Wakeham, The Viscosity of 5 Liquid Hydrocarbons at Pressures up to 250 MPa, *Int. J. Thermophys.*, 13 (1992) 773-790.
- [54] A.F. Collings, E. McLaughlin, Torsional Crystal Technique for the Measurement of Viscosities of Liquids at High Pressures, *Trans. Faraday Soc.*, 67 (1971) 340-352.
- [55] D.W. Brazier, G.R. Freeman, The effects of pressure on the density, dielectric constant, and viscosity of several hydrocarbons and other organic liquids, *Can. J. Chem.*, 47 (1969) 893-899.
- [56] J. Dymond, K.J. Young, J.D. Isdale, Transport Properties of Nonelectrolyte Liquid Mixtures. II. Viscosity Coefficients for the n-Hexane - n-Hexadecane System at Temperatures from 25 to 100 C at Pressures up to the Freezing Pressure or 500 MPa, *Int. J. Thermophys.*, 1 (1980) 345-373.
- [57] J.D. Isdale, J. Dymond, T.A. Brawn, Viscosity and Density of n-Hexane-Cyclohexane Mixtures Between 25 and 100 C up to 500 MPa, *High Temperature Science*, 11 (1979) 571-580.
- [58] M.J. Assael, M. Papadaki, Measurements of the Viscosity of n-Heptane, n-Nonane, and n-Undecane at Pressures up to 70 MPa, *Int. J. Thermophys.*, 12 (1991) 801-810.
- [59] M.J. Assael, C.P. Oliveira, M. Papadaki, W.A. Wakeham, Vibrating-Wire Viscometers for Liquids at High-Pressures, *Int. J. Thermophys.*, 13 (1992) 593-615.
- [60] M.J. Assael, E. Charitidou, J.H. Dymond, M. Papadaki, Viscosity and Thermal-Conductivity of Binary Normal-Heptane + Normal-Alkane Mixtures, *Int. J. Thermophys.*, 13 (1992) 237-249.
- [61] C.K. Zeberg-Mikkelsen, G. Watson, A. Baylaucq, G. Galliero, C. Boned, Comparative experimental and modeling studies of the viscosity behavior of ethanol+C7 hydrocarbon mixtures versus pressure and temperature, *Fluid Phase Equilib.*, 245 (2006) 6-19.
- [62] D.R. Caudwell, J.P.M. Trusler, V. Vesovic, W.A. Wakeham, Viscosity and Density of Five Hydrocarbon Liquids at Pressures up to 200 MPa and Temperatures up to 473 K, *J. Chem. Eng. Data*, 54 (2009) 359-366.
- [63] K.R. Harris, R. Malhotra, L.A. Woolf, Temperature and density dependence of the viscosity of octane and toluene, *J. Chem. Eng. Data*, 42 (1997) 1254-1260.
- [64] J.H. Dymond, J. Robertson, J.D. Isdale, Transport Properties of Nonelectrolyte Liquid Mixtures - 3. Viscosity Coefficients for n-Octane, n-Dodecane, and Equimolar Mixtures Of n-Octane + n-Dodecane and n-Hexane + n-Dodecane From 25 to 100 °C at Pressures up to the Freezing Pressure or 500 MPa, *Int. J. Thermophys.*, 2 (1981) 133-154.
- [65] Y. Tanaka, H. Hosokawa, H. Kubota, T. Makita, Viscosity and Density of Binary-Mixtures of Cyclohexane with N-Octane, N-Dodecane, and N-Hexadecane under High-Pressures, *Int. J. Thermophys.*, 12 (1991) 245-264.
- [66] M.J. Assael, J.H. Dymond, M. Papadaki, Viscosity Coefficients of Binary N-Heptane+N-Alkane Mixtures, *Fluid Phase Equilib.*, 75 (1992) 287-297.
- [67] L.T. Carmichael, V.M. Berry, B.H. Sage, Viscosity of Hydrocarbons. n-Decane, *J. Chem. Eng. Data*, 14 (1969) 27-31.
- [68] F. Audonnet, A.A.H. Padua, Viscosity and density of mixtures of methane and n-decane from 298 to 393 K and up to 75 MPa, *Fluid Phase Equilib.*, 216 (2004) 235-244.
- [69] K. Rajagopal, L.L.P.R. Andrade, M.L.L. Paredes, High-Pressure Viscosity Measurements for the Binary System Cyclohexane plus n-Hexadecane in the Temperature Range of (318.15 to 413.15) K, *J. Chem. Eng. Data*, 54 (2009) 2967-2970.
- [70] D.R. Caudwell, J.P.M. Trusler, V. Vesovic, W.A. Wakeham, The Viscosity and Density of N-Dodecane and N-Octadecane at Pressures up to 200 MPa and Temperatures up to 473 K, *Int. J. Thermophys.*, 25 (2004) 1339-1352.
- [71] D.L. Hogenboom, W. Webb, J.A. Dixon, Viscosity of Several Liquid Hydrocarbons as a Function of Temperature, Pressure, and Free Volume, *J. Chem. Phys.*, 46 (1967) 2586-2598.
- [72] F. Ijaz, Measurement and Prediction of the Viscosity of Hydrocarbon Mixtures and Crude Oils, PhD Thesis, Imperial College London, 2011.
- [73] C.K. Zeberg-Mikkelsen, M. Barrouhou, A. Baylaucq, C. Boned, Measurements of the viscosity and density versus temperature and pressure for the binary system methylcyclohexane+2,2,4,4,6,8,8-heptamethylnonane, *High Temp-High Press*, 34 (2002) 591-601.
- [74] X. Canet, P. Dauge, A. Baylaucq, C. Boned, C.K. Zeberg-Mikkelsen, S.E. Quinones-Cisneros, E.H. Stenby, Density and viscosity of the 1-methylnaphthalene + 2,2,4,4,6,8,8-

heptamethylnonane system from 293.15 to 353.15 K at pressures up to 100 MPa, *Int. J. Thermophys.*, 22 (2001) 1669-1689.

[75] E.W. Lemmon, M.L. Huber, M.O. McLinden, NIST Standard Reference Database 23: Reference Fluid Thermodynamic and Transport Properties-REFPROP, in, National Institute of Standards and Technology, Gaithersburg, 2013.

[76] U. Setzmann, W. Wagner, A New Equation of State and Tables of Thermodynamic Properties for Methane Covering the Range from the Melting Line to 625-K at Pressures up to 1000-Mpa, *J. Phys. Chem. Ref. Data*, 20 (1991) 1061-1155.

[77] D. Bucker, W. Wagner, A reference equation of state for the thermodynamic properties of ethane for temperatures from the melting line to 675 K and pressures up to 900 MPa, *J. Phys. Chem. Ref. Data*, 35 (2006) 205-266.

[78] D. Bucker, W. Wagner, Reference equations of state for the thermodynamic properties of fluid phase n-butane and isobutane, *J. Phys. Chem. Ref. Data*, 35 (2006) 929-1019.

[79] E.W. Lemmon, M.O. McLinden, W. Wagner, Thermodynamic Properties of Propane. III. A Reference Equation of State for Temperatures from the Melting Line to 650 K and Pressures up to 1000 MPa, *J. Chem. Eng. Data*, 54 (2009) 3141-3180.

[80] R. Span, W. Wagner, Equations of state for technical applications. II. Results for nonpolar fluids, *Int. J. Thermophys.*, 24 (2003) 41-109.

[81] P.A. Vicharelli, Analytic Parametrization of Transport-Coefficients of Lennard-Jones (N,6) Fluids, *J Appl Phys*, 62 (1987) 2250-2255.

[82] R.S. Brokaw, NASA Technical Report R-81, in, Washington D.C., 1960.

[83] F. Peleties, J.P.M. Trusler, Viscosity of Liquid Di-isodecyl Phthalate at Temperatures Between (274 and 373) K and at Pressures up to 140 MPa, *J. Chem. Eng. Data*, 56 (2011) 2236-2241.

[84] K.R. Harris, S. Bair, Temperature and pressure dependence of the viscosity of diisodecyl phthalate at temperatures between (0 and 100) degrees C and at pressures to 1 GPa, *J. Chem. Eng. Data*, 52 (2007) 272-278.

[85] K.R. Harris, Temperature and Pressure Dependence of the Viscosities of 2-Ethylhexyl Benzoate, Bis(2-ethylhexyl) Phthalate, 2,6,10,15,19,23-Hexamethyltetracosane (Squalane), and Diisodecyl Phthalate, *J. Chem. Eng. Data*, 54 (2009) 2729-2738.

[86] F. Peleties, J.J. Segovia, J.P.M. Trusler, D. Vega-Maza, Thermodynamic properties and equation of state of liquid di-isodecyl phthalate at temperature between (273 and 423) K and at pressures up to 140 MPa, *J Chem Thermodyn*, 42 (2010) 631-639.