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An Improved Correlation for the Viscosity of Simple Fluids at High Densities

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Dedicated to Professor Klaus Gersten on the Occasion of His 60th Birthday

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The Batschinski–Hildebrand relation is improved by plotting the fluidity versus the molar volume minus the hard-core volume of the molecules, the latter given by equation of state calculations. The relation can be cast in a corresponding states form by reducing the fluidity by the molar mass, the critical temperature, and the critical volume and by reducing the volume by the zero temperature hard-core volume. The random close-packed volume, where the fluidity is zero, is in reasonable agreement with theoretical considerations of hard spheres. The small deviations from corresponding states for liquids are interpreted either by polarity or by nonconvexity of the molecules.

KEY WORDS: fluidity; hard-core volume; high density; random closed packing; reduced viscosity.

1. INTRODUCTION

Batschinski [1] and later Hildebrand and Lamoreaux [2] have shown that the reciprocal viscosity, the fluidity, is for dense liquids a linear function of molar volume. This might not be true for very small fluidities as in the case of more complicated hydrocarbons at low reduced temperatures [3], but it is a good approximation for a relatively large range in fluidity. Closer inspection shows that a plot of fluidity versus molar volume for compressed liquid isotherms does not give a straight line, but a series of steps where each step corresponds to a given temperature. This is demonstrated for the example of benzene in Fig. 1. The idea suggests itself to subtract from the volume something like the molecular volume, which

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is a weak function of temperature. Indeed, if the hard-core volume of benzene is subtracted as given by the equation of state [4–6], a straight line emerges (Fig. 2).

When the same procedure is done for different liquids, the individuality of the resulting lines can be greatly reduced by emploing reduced fluidities

$$\eta_r^{-1} = \frac{0.0108(MT_c)^{1/2}}{\eta v_c^{2/3}} \tag{1}$$

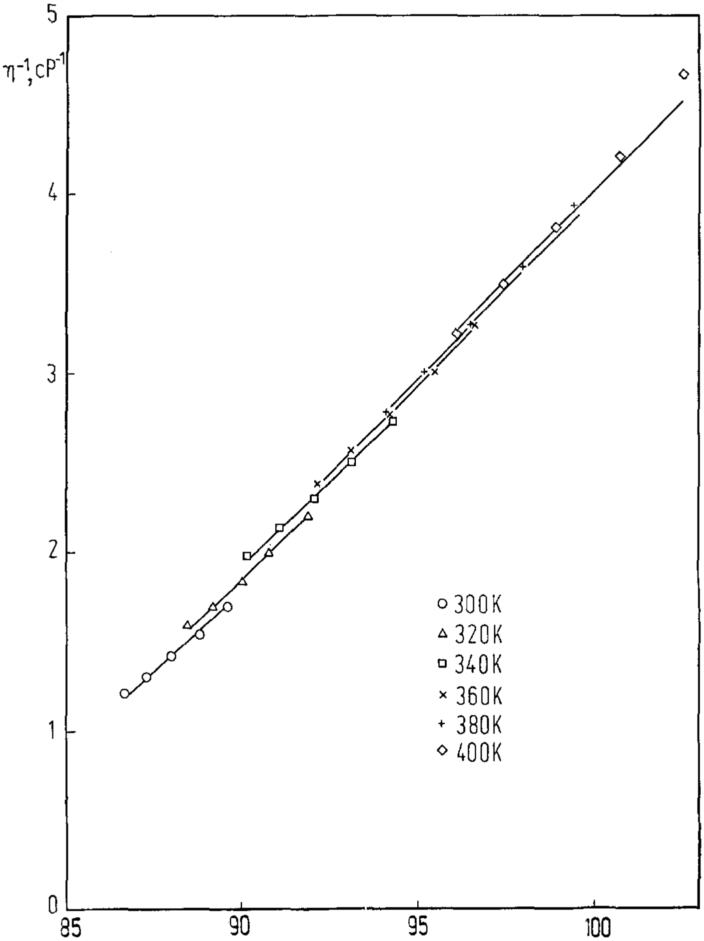

Fig. 1. The fluidity of benzene versus the molar volume (1 cP = 1 mPa · s).

and plotting these versus $(v - v^*)/v_0^*$, where v, v^*, and v_0^* are the molar volume, the volume of 1 mol of hard bodies at the appropriate temperature, and the volume of 1 mol of hard bodies at zero temperature. The factor in Eq. (1) is appropriate when η is expressed in cP(=mPa · s), the critical volume v_c in $cm^3 \cdot mol^{-1}$, T_c in K, and the molar mass in $g \cdot mol^{-1}$. Of special interest is the value where the extrapolated straight lines intersect with the abscissa, as zero fluidity means random close packing from a

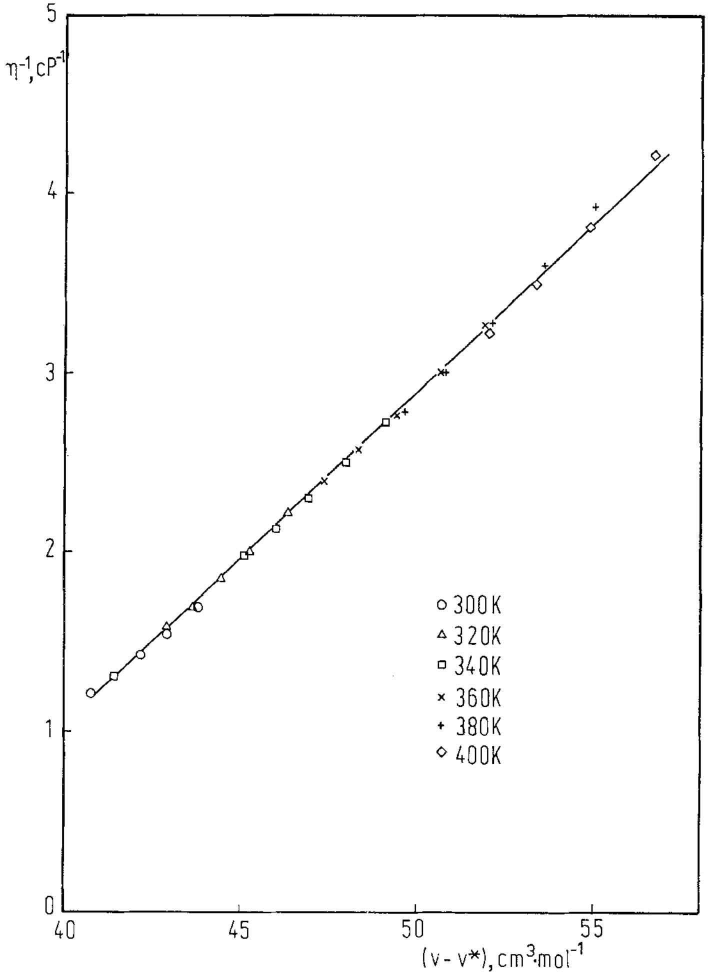

Fig. 2. Same as Fig. 1, but the molar volume diminished by the molecular hard-core volume.

Table I. Coefficients Used in Eq. (3)

K_1	0.23833208
K_2	1.2849269
K_3	0.23760582
K_4	0.51973232
N	50

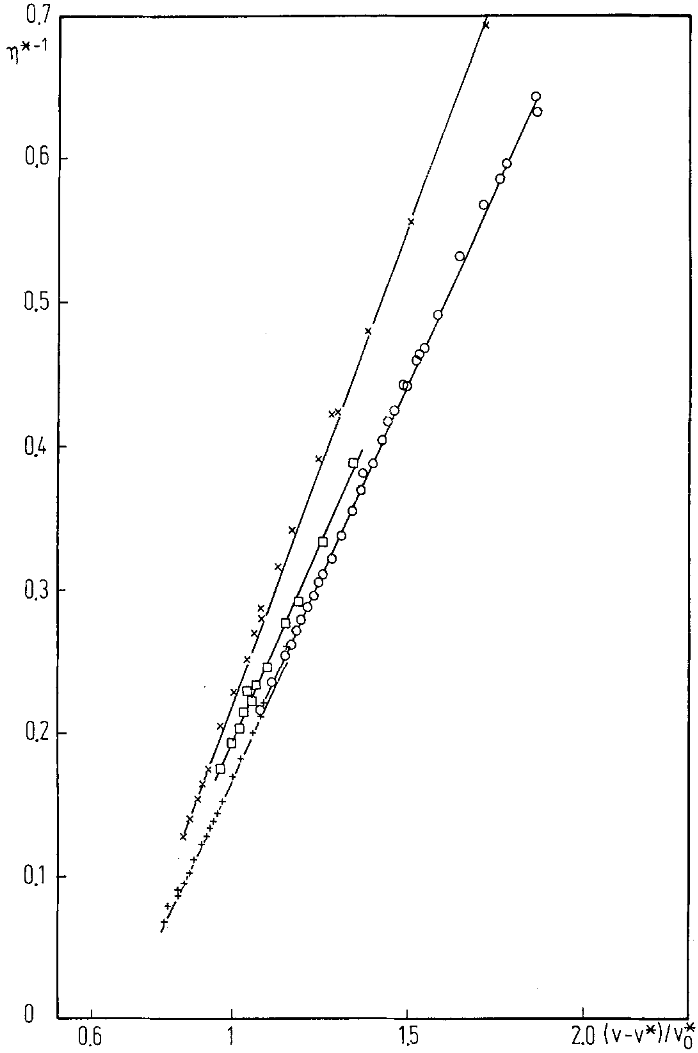

Fig. 3. The reduced fluidity η^{*-1} of argon (○), methane (×), pentane (□), and benzene (+). Solid lines correspond to the correlation Eq. (2).

kinematic point of view. In this circumstance, temperature will be practically zero, so that Eq. (1) could be written

$$\eta_r^{-1} = A\left\{\frac{v - v^*}{v_0^*} - \frac{v_{\rm rcp} - v_0^*}{v_0^*}\right\} \tag{2}$$

where $v_{\rm rcp}$ means molar volume for random close packing. It is the purpose of this paper to evaluate the parameters A and $v_{\rm rcp}/v_0^*$ for a number of substances and to compare them with molecular properties.

It should be noted that the present approach has some similarities to a calculation presented by Li et al. [7] on alkanes (ethane to octane). Significant differences are that here the volume to be subtracted, v^*, is determined by the equation of state and that the reduced viscosity is formed with the critical volume and the critical temperature, whereas Li et al. employed the actual volume and the actual temperature. Our way of reducing the viscosity goes back to Mazo [8] and is briefly outlined in the book by Kohler [9]. It has been employed by, among others, Teja and Rice [10].

2. RESULTS

The only parameter from equation of state calculations entering into the present treatment is the hard-core volume v^*. Initially, this parameter

Table II. The Coefficients of Eq. (2), the Averaged Relative Deviation from the Fitted Line, and the Relation of the Zero Temperature Hard-Core Volume to the Critical Volume, for the Substances Investigated

Substance	A	$v_{\rm rcp}/v_0^*$	Ave. error (%)	v_0^*/v_c
Ar	0.545	1.683	0.704	0.1978
N_2	0.564	1.681	0.956	0.1993
O_2	0.576	1.643	0.724	0.1985
CH_4	0.672	1.674	1.308	0.2004
C_2H_6	0.524	1.580	2.419	0.1998
C_3H_8	0.548	1.651	0.994	0.1979
C_4H_{10}	0.543	1.643	1.131	0.1991
C_5H_{12}	0.546	1.639	2.450	0.1982
C_6H_6	0.531	1.680	1.007	0.1974
C_3H_6	0.535	1.696	0.407	0.1903
CO_2	0.592	1.787	1.238	0.1941
R22	0.577	1.701	1.266	0.1868
NH_3	0.616	1.785	0.346	0.1707

was fitted for each isotherm to the liquid densities. But it has been found that it follows a universal function of the reduced temperature for all substances with the zero-temperature point hard-core volume as a single individual parameter:

$$v^* = v_0^* \left[\left(\frac{1}{1 + K_1 (T/T_c)^{K2}} \right)^N + \left(\frac{1}{1 + K_3 (T/T_c)^{K4}} \right)^N \right]^{1/N} \tag{3}$$

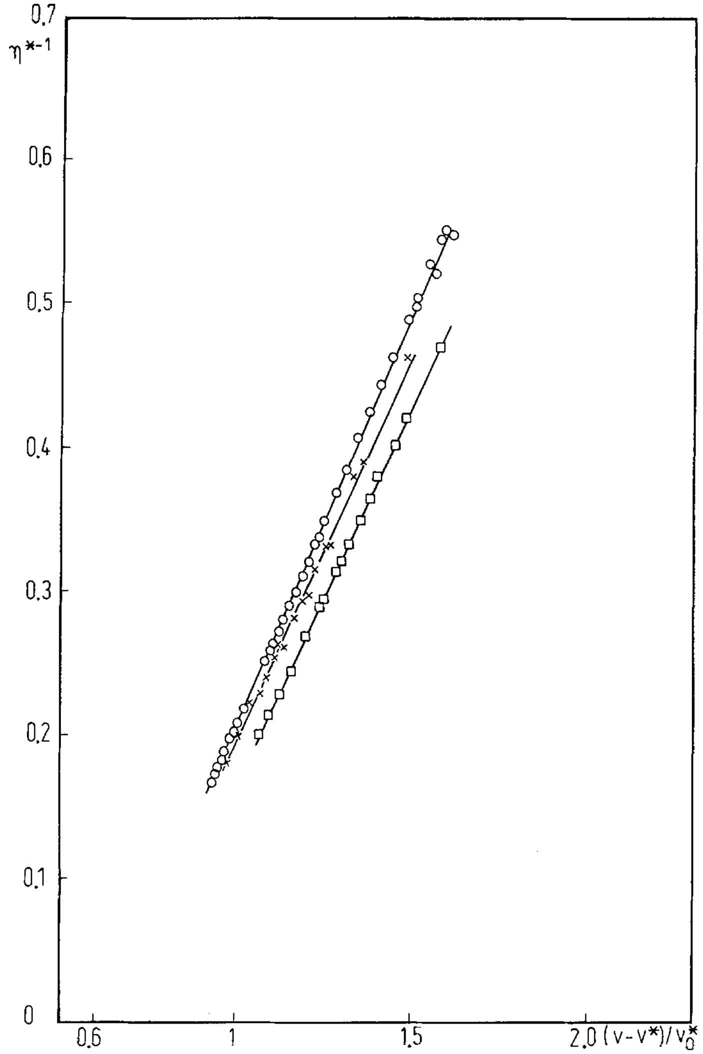

Fig. 4. Same as Fig. 3, but for oxygen (○), butane (×), and propene (□).

The universal coefficients are given in Table I. Equation (3) is very similar to the function presented previously [6] but shows some improvement around T_c.

Before discussing the calculations on the individual substances, an overview is given in Table II, where the parameters A and v_{rcp}/v_0^* are summarized. In addition, the averaged relative deviation of the experimental

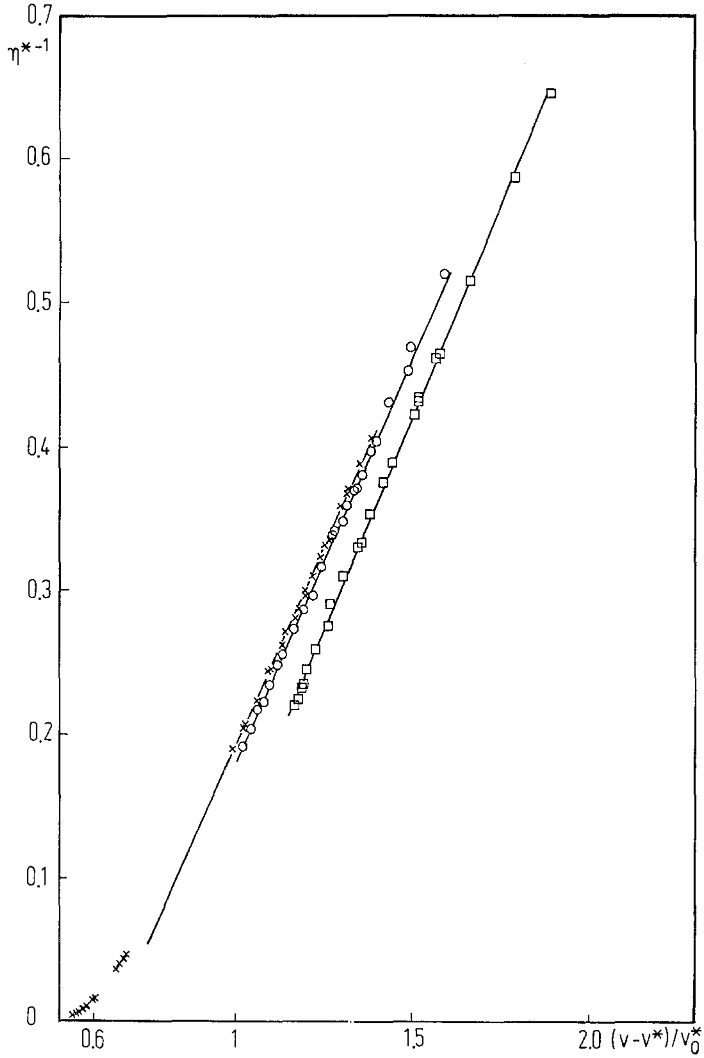

Fig. 5. Same as Fig. 3, but for propane (×), nitrogen (○), and carbon dioxide (□).

points from the fitted straight line is listed. Finally, in the last column, the ratio of the zero-point hard-core volume to the critical volume is listed. This last column demonstrates the consistency of the equation of state calculations for nonpolar fluids, which exceeds significantly the consistency of the A and v_{rcp}/v_0^* parameters. This shows that molecular properties influence the fluidity in ways slightly different from the equilibrium quantities.

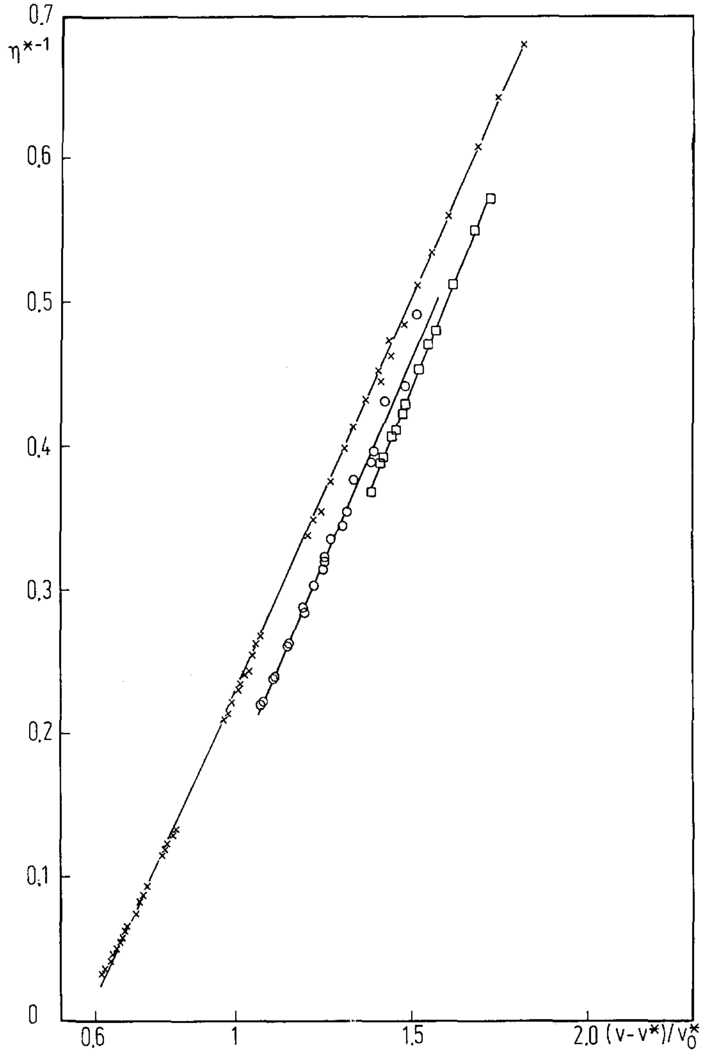

Fig. 6. Same as Fig. 3, but for ethane (×), monochlorodifluoromethane (R22) (○), and ammonia (□)

Table III. References for the Experimental Quantities Used

Substance	T_c (K)	v_c ($cm^3 \cdot mol^{-1}$)	Ref. No.	Temp. range (K)	Ref. No. for η
Ar	150.6633	75.2445	22	108–173	34
N_2	126.193	89.4694	23	90–120	35
O_2	154.581	73.3681	24,25	90–150	36
CH_4	190.551	98.6291	13	100–170	30
C_2H_6	305.420	146.2416	14,15	100–290	31
C_3H_8	369.85	201.8163	16,17	250–320	32–33
C_4H_{10}	425.14	255.1020	16,18	280–360	33
C_5H_{12}	469.69	310.9936	16,19	320–380	33
C_6H_6	562.16	256.9967	21	300–400	33
C_3H_6	365.57	188.3736	20	290–310	33
CO_2	304.136	94.1168	26	220–280	37
R22	369.3	173.1602	27	270–320	33
NH_3	405.50	72.4638	28,29	310–340	33

The theoretical value for v_{rcp}/v_0^* for a hard-sphere liquid is known only with some uncertainty. The quantity extrapolated from old computer experiments is 1.554 [11, 12]. But a "glass transition" has been postulated in the hard-sphere liquid already at $v/v_0^* = 1.675$ [12]. The values in Table II are at least reasonable.

The calculations on the individual substances are illustrated by Figs. 3–6, with the references listed in Table III. The fit is done over the temperature range indicated, whereas low-temperature points are included in the figures for ethane and propane which deviate to higher values in the same way as was shown for hexane in Ref. 3. If one considers nonpolar substances (Ar to propene), the A value is $\pm$ the same (0.550 ± 0.025), the only exception being methane. The reduced random close-packed volume is around 1.68 for Ar, CH_4, and N_2, is lowered to 1.64–1.65 for the C_3–C_5 alkanes and oxygen, and goes down to 1.58 for ethane. For the quadrupolar and dipolar molecules the value is increased up to 1.79. With this increase there is a parallel increase in the A parameter.

This last result can be readily understood. Local electric moments hinder the motion of the molecules, and this increases v_{rcp}/v_0^*. At higher temperatures, this hindrance is less pronounced, and this increases the A parameter. However, inspection of the figures shows that also at higher temperatures the fluidity of the polar liquids is reduced. The effect of polarity (quadrupolar or dipolar) is also revealed, though in a different way, by the ratio v_0^*/v_c.

It is more difficult to speculate about the reduction of the random close-packed volume for the alkanes. It seems that this has to do with the nonconvexity of the molecular body, causig the kinematic hard-core volume to be smaller than the equilibrium hard-core volume. This is most pronounced for ethane, where all six H atoms are directed away from the C–C bond, leaving a narrowing of the molecular body at the center. For methane, the nonconvexity might be present only at higher temperature, when the region between H atoms can be penetrated. Perhaps this is the cause for the anomalous A value.

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