

# Correlation for the Viscosity of Normal Hydrogen Obtained from Symbolic Regression

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**ABSTRACT:** We report the results of a symbolic-regression methodology to obtain both the functional form and the coefficients for a wide-ranging correlation for the viscosity of normal hydrogen. The correlation covers the temperature range from the triple-point temperature to 1000 K and pressures up to 200 MPa and extrapolates in a physically reasonable manner to 2000 K. The estimated uncertainty is 4 % for the saturated liquid from the triple point to 31 K, with larger deviations as the critical region is approached. The estimated uncertainty is 4 % for the supercritical fluid phase at pressures to 200 MPa. For the limited range of 200 K to 400 K at pressures up to 0.1 MPa, the uncertainty is 0.1 %.



# INTRODUCTION

Recent interest in reducing petroleum usage, lowering greenhouse gas emissions, improving air quality, and developing a more diverse energy infrastructure has led to renewed interest in hydrogen as a fuel and as an energy carrier. To advance new hydrogen technologies, it is important to have accurate thermophysical property information. Deficiencies identified<sup>1</sup> in currently available formulations for the viscosity surface<sup>2,3</sup> present an opportunity to provide an improved correlation. In addition, a powerful new technique, symbolic regression,<sup>4</sup> has become available to identify underlying trends in experimental data. The purpose of this work is to demonstrate the use of symbolic regression to develop correlations of material properties. In particular, we developed an improved, wide-ranging correlation for the viscosity of hydrogen.

The viscosity  $\eta(\rho,T)$  of a fluid can be expressed as the sum of independent contributions, as<sup>S</sup>

$$\eta(\rho, T) = \eta_{o}(T) + \Delta \eta_{excess}(T, \rho) + \Delta \eta_{c}(\rho, T)$$
(1)

$$\Delta \eta_{\text{excess}}(\rho, T) = \eta_{\text{l}}(T)\rho + \Delta \eta_{\text{h}}(\rho, T)$$
(2)

Here, the first term,  $\eta_o(T) = \eta(0,T)$ , is the contribution to the viscosity in the limit of zero density, where only two-body molecular interactions occur. The term  $\Delta \eta_{\text{excess}}(T,\rho)$  accounts for the increase in viscosity above the zero-density value at elevated density, and it can be expressed in terms of an initial-density viscosity coefficient  $\eta_1(T)$  and a term  $\Delta \eta_h(\rho,T)$  representing the contribution of all other higher-order effects to the viscosity of the fluid at elevated densities including many-body collisions, molecular-velocity correlations, and collisional transfer. The term,  $\Delta \eta_c(\rho,T)$ , the critical enhancement, arises from the long-range fluctuations that occur in a fluid near its

critical point that contribute to a weak divergence of the viscosity at the critical point.  $^{6}$ 

The identification of these distinct contributions to the viscosity is useful because it is possible, to some extent, to treat  $\eta_o(T)$ ,  $\eta_1(T)$ , and  $\Delta \eta_c(\rho,T)$  theoretically. Unlike the critical contribution to the thermal conductivity that impacts a relatively large region of temperatures and densities around the critical point, the critical contribution to the viscosity is limited to a very small region in close proximity of the critical point.<sup>6</sup> For several fluids where there are sufficient data in the critical region, it has been shown<sup>7,8</sup> that the ratio of  $\Delta \eta_c/\eta$  is greater than 0.01 only within 1 % of the critical temperature. In this work, we will omit the critical contribution and consider only data outside of 1 % of the critical temperature and not near the critical pressure. Kinetic theory can be used to calculate the zero-density viscosity.<sup>9</sup> In particular, advances in theory have led to accurate calculations of the dilute-gas viscosity that can be used to supplement experimental values. Mehl et al.<sup>10</sup> presented quantum mechanical ab initio calculations of the dilute-gas viscosity and thermal conductivity of normal hydrogen and parahydrogen. Rainwater and Friend<sup>11</sup> presented a theory for the calculation of  $\eta_1(T)$ . However, there is almost no theoretical guidance concerning the contribution,  $\Delta \eta_{\rm h}(\rho,T)$ , so that its evaluation is based entirely on experimentally obtained data. The goal of this work is to apply a symbolic-regression methodology to this term to identify a functional form that best represents the experimental data.

Received: November 30, 2012 Accepted: March 7, 2013 Published: March 27, 2013



# Table 1. Summary of Available Data<sup>a</sup>

first author	year	method	purity/%	est. unc./%	no. pts.	T range/K	p range/MPa
Breitenbach <sup>32</sup>	1901	CAP	na	na	5	252 to 575	0.1
Markowski <sup>33</sup>	1904	CAP	na	na	3	287.6 to 457.3	0.1
Schmitt <sup>34</sup>	1909	TRANSP	na	na	10	78.3 to 458.4	0.1
Kamerlingh Onnes <sup>35</sup>	1913	CAP	na	2	17	20 to 294	0.03 to 0.06
Vogel <sup>36</sup>	1914	OD	na	na	7	21 to 273.1	0.01 to 0.1
Gille <sup>37</sup>	1915	CAP	na	na	7	273 to 373	0.1
Verschaffelt <sup>38</sup>	1917	unknown	na	1	1	20.35	0.1
Yen <sup>39</sup>	1919	CD	na	na	1	296.1	0.1
Gunther <sup>40</sup>	1920	SWP	na	na	8	15 to 273	0.01 to 0.1
Ishida <sup>41</sup>	1923	OIL	na	0.3	1	321	0.1
Klemenc <sup>42</sup>	1923	TRANSP	na	na	1	273	0.1
Gunther <sup>43</sup>	1924	SWP	na	na	16	15 to 273	0.01 to 0.1
Trautz <sup>44</sup>	1929	TRANSP	na	na	12	195.2 to 523.2	0.1
Trautz <sup>45</sup>	1929	TRANSP	na	na	20	288.6 to 523.6	0.1
Trautz <sup>40</sup>	1929	TRANSP	na	na	15	192.4 to 524.9	0.1
Boyd <sup>T</sup>	1930	TRANSP	na	na	56	303 to 343	7.2 to 19.4
Trautz <sup>10</sup>	1930	TRANSP	na	na	6	298.2 to 523.2	0.1
Trautz <sup>50</sup>	1930	TRANSP	na	na	8	293.1 to 523.4	0.1
Trautz <sup>50</sup>	1930	TRANSP	na	na	8	289.8 to 1099.0	0.1
$T_{rautz}^{52}$	1931	TRANSP	na	na	12	295.2 to 523.4	0.1
Trautz <sup>53</sup>	1931	TRANSP	na	na	12	300.0 to 551.2	0.1
Trautz	1931	TRANSP	na	na	12	292.6 to \$23.2	0.1
Sutherland Ciliar a <sup>55</sup>	1932	UD	na	0.4	11	74.8 to 293.8	0.1
Gibson <sup>-1</sup>	1933	TRANSP TRANSP	99.9	0.4	20	298 202 hr 522	1.1 to 29.9
Trautz <sup>57</sup>	1934	TRANSP TRANSP	na	na	4	293 to 523	0.1
riautz	1955	I KAINSP OD	na		1	90 205	0.1
A drum i <sup>59</sup>	1935	OD CAD	na	0.2	1	295 202 to 272	0.1
Adzumi Kassam <sup>60</sup>	1937	CAP	na	na 2	9	293 to 3/3	0.1
van Ittarhaalr <sup>61,62</sup>	1930	OD OD	na	2	14	14.5 to 20.5	$0.01 \ 10 \ 0.1$
Johns <sup>27</sup>	1930	CAP	na	11a 1 1	11	14 to 292.9	0 10 0.01
Johnston <sup>63</sup>	1939	OD	na	1.1	74 24	90 to 300	0.13  to  0.23
Keesom <sup>64</sup>	1940	OD	na	0.5 10 0.7	24	13 9 to 20 5	0.02  to  0.1
van Itterbeek <sup>65</sup>	1940	OD	na	2	30	14.9 to 2025	0.01 to 0.1
van Itterbeek <sup>66</sup>	1940	OD	na	na	6	14.9 to 291.8	0.01 to $0.1$
van Itterbeek <sup>67</sup>	1941	OD	na	na	5	14.7  to  20.4	0.01 to 0.1
Wobser <sup>68</sup>	1941	HOP viscometer	na	na	5	293 1 to 371 2	0.1
Buddenberg <sup>69</sup>	1951	CAP	99 99	na	7	293 to 301	0.1
Kuss <sup>28</sup>	1952	CAP	na	2	27	298-348	0.1 to 49
Kompaneets <sup>70</sup>	1953	CAP	na	na –	-7	284 to 873	0.1
Michels <sup>22</sup>	1953	CAP	na	0.2 <sup>b</sup>	95	298.1 to 398.1	2.6 to 186.3
Kestin <sup>71</sup>	1954	OD	99.99	0.2	1	294	0.1
Rietveld <sup>72</sup>	1957	OD	na	na	7	14.4 to 293.1	0 to 0.004
Coremans <sup>73</sup>	1958	OD	na	2 <sup><i>b</i></sup>	14	20 to 78	0.1
Kestin <sup>74</sup>	1958	OD	99.992	0.2	10	298	0.1 to 7.1
Kestin <sup>75</sup>	1959	OD	99.974	0.05	9	293	0.4 to 8.4
Rietveld <sup>76</sup>	1959	OD	na	3	14	14.4 to 293.1	0.0005 to 0.005
Kestin <sup>77</sup>	1963	OD	99.999	0.2	13	293 to 303	0.1 to 0.6
Rudenko <sup>78</sup>	1963	CAP	na	1.3	8	14.5 to 20.4	0.01 to 0.1
Barua <sup>79</sup>	1964	CAP	99.96	0.2	38	223 to 423	0.8 to 15.0
Diller <sup>17c</sup>	1965	TORC	na	0.5	13	14 to 26	sat liquid
Diller <sup>17e</sup> (parahydrogen) <sup>17</sup>	1965	TORC crystal	na	0.5	320	15 to 100	0.04 to 31.7
Menabde <sup>80</sup>	1965	OD	na	$2^{b}$	11	77.4 to 299.6	0.006
Tsederberg <sup>30</sup>	1965	CAP	na	3	28	288.6 to 990.4	4.4 to 50.6
Golubev <sup>81</sup>	1966	CAP	99.99	1	96	77 to 273	0.9 to 49.1
Andreev <sup>82</sup>	1967	CAP	99.7	1.5	11	293	0.1 to 49
Konareeva <sup>83</sup>	1967	TOROC	na	1.5	10	14 to 32	0 to 1
Kestin <sup>84</sup>	1968	OD	99.999	0.2	13	293 to 303	0 to 2.4
Rudenko <sup>85d</sup>	1968	FB	na	1.5	91	33.2 to 300	0.1 to 217.1
Gracki <sup>86</sup>	1969	CAP	99.95	0.2	42	173 to 298	0.4 to 17.1
Guevara <sup>23</sup>	1969	САР	na	$2^{b}$	23	1103 to 2152	0.1

#### Table 1. continued

first author	year	method	purity/%	est. unc./%	no. pts.	T range/K	p range/MPa
Golubev <sup>87</sup>	1970	САР	na	na	58	298 to 523	0.1 to 81.6
Kestin <sup>88</sup>	1971	OD	99.9995	0.1	3	295 to 308	0.1
Carey <sup>89</sup>	1974	ACST	na	0.1	18	291 to 299	0.15 to 11
Chuang <sup>90</sup>	1976	CAP	99.999	0.5	37	173 to 273	0.4 to 50.6
Clifford <sup>21</sup>	1981	OD	99.9995	0.2	2	298 to 308	0.1
Lukin <sup>91</sup>	1983	CAP	na	0.3	23	76.5 to 293.2	0.1
Nabizadeh <sup>12</sup>	1999	OD	na	0.5 to 1	76	295.6 to 399.2	0.1 to 5.8
Maltsev <sup>13</sup>	2004	CAP	99.9	3	3	500 to 1100	0.3
May <sup>14</sup>	2007	2CAP	99.9999	0.08	32	213.6 to 394.2	0 to 0.11
Mehl <sup>10</sup>	2010	ab initio calculations	na	0.08 to 10	20	20 to 2000	0
Hurly <sup>15</sup>	2011	GRN	99.9999	0.5	111	225 to 400	0.3 to 3.4
Yusibani <sup>16</sup>	2011	CAP	99.999	2	17	294 to 400	4.6 to 99.3

<sup>*a*</sup>Abbreviations: est. unc., estimated uncertainty; no. pts., number of points; na, not available; 2CAP, twin capillary; ACST, acoustic resonance; CAP, capillary; CD, constant deflection; FB, falling body; GRN, Greenspan viscometer; HOP, Hoppler viscometer; OIL, oil drop; OD, oscillating disc; SWP, swinging plate; TOROC, torsional oscillating cylinder; TORC, torsional crystal; TRANSP, transpiration. Values in bold type are considered primary data. <sup>*b*</sup>Uncertainty ascribed by Assael et al.<sup>20</sup> <sup>*c*</sup>Isotherms (32 K) close to critical excluded from primary data set. <sup>*d*</sup>Only points above 150 K considered in primary data set. <sup>*e*</sup>Parahydrogen; data adjusted as described in text.

## EXPERIMENTAL DATA

Previously, Leachman et al.<sup>1</sup> reviewed the experimental viscosity data for normal and parahydrogen current to 2006.





Figure 1. Temperature and density ranges of the experimental data.

### Figure 2. Temperature and pressure ranges of the experimental data.

#### Table 2. Coefficients of Equation 4





**Figure 3.** Deviations of eqs 3 and 4 from the primary data and selected secondary data for dilute gas.

Table 1 summarizes the presently available data for the viscosity of normal hydrogen, including the measurement method, range of experimental conditions, and an estimate of the experimental uncertainty. The uncertainties are those supplied by the original authors, except where noted. In many cases these estimates are highly optimistic. There are few recent measurements; since 1990, only five new data sets have appeared in the literature.<sup>12–16</sup> Owing to the scarcity of reliable low-temperature data, we supplemented the normal hydrogen data with the parahydrogen measurements of Diller<sup>17</sup> that were adjusted by first calculating their densities with the Leachman equation

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Figure 4. Deviations of eqs 3 and 4 from literature correlations for zero-density viscosity.

Table 3. Coefficients of Equation 7<sup>92</sup>

i	$\boldsymbol{b}_i$
0	-0.1870
1	2.4871
2	3.7151
3	-11.0972
4	9.0965
5	-3.8292
6	0.5166

#### Table 4. Coefficients of Equation 9

i	$c_i$
1	6.43449673
2	4.56334068.10 <sup>-02</sup>
3	$2.32797868 \cdot 10^{-01}$
4	9.58326120.10 <sup>-01</sup>
5	$1.27941189 \cdot 10^{-01}$
6	$3.63576595 \cdot 10^{-01}$

of state for parahydrogen,<sup>18</sup> and then recalculating an equivalent normal-hydrogen pressure with the Leachman equation of state for normal hydrogen.<sup>18</sup> This has the effect of assuming that the parahydrogen viscosity is essentially equivalent to normal hydrogen viscosity provided that the density is the same. Figures 1 and 2 display the data sets and illustrate the range of data coverage in the  $T,\rho$  and T,p planes, respectively.

We evaluated the data and assigned data to either a primary or secondary data set. Data considered as primary (indicated by bold type in Table 1) were used in the development of the correlation, while secondary data were used only for comparison purposes. The Subcommittee on Transport Properties (now known as The International Association for Transport Properties) of the International Union of Pure and Applied Chemistry made recommendations for the selection of primary data for fluid transport properties. These recommendations include<sup>19</sup> that the measurements must have been made with a primary experimental apparatus, that is, one for which a complete working equation is available; the form of the working equation should be such that sensitivity of the property measured to the principal variables does not magnify the random errors of measurement; all principal variables should be measurable to a high degree of precision; there should be information on sample purity or purification methods; and explicit quantitative estimates of the uncertainty of reported values should be given, taking into account the precision of experimental measurements and possible systematic errors. Unfortunately, very few data in Table 1 meet these standards. Consequently, within the primary data set it is also necessary to include results that extend over a wide range of conditions, albeit with a poorer accuracy, provided that they cannot be demonstrated to be inconsistent with other more accurate data or with theory. In all cases, the accuracy claimed for the final recommended data must reflect the estimated uncertainty in the primary information.

Assael et al.<sup>20</sup> reviewed the experimental data available for the development of a dilute-gas correlation for hydrogen. Since the time of that publication, May et al.<sup>14</sup> provided very high accuracy experimental data for the zero-density viscosity of hydrogen over the temperature range 200 K to 400 K. We selected these data for the primary data set for this temperature range since it has a much lower uncertainty (0.08 %) than the data previously considered<sup>21,22</sup> by Assael et al.<sup>20</sup> For the highest temperatures (above 1100 K), we selected the measurements of Guevara et al.<sup>23</sup> In addition, to supplement the experimental data, we included as primary data the theoretical values from Mehl et al.<sup>10</sup> who employed the spherical version of the hydrogen intermolecular potential determined in ab initio calculations by Patkowski et al.<sup>24</sup> to calculate the viscosity of normal and parahydrogen using a full quantum-mechanical formalism. Comparisons of the *ab initio* values with the experimental data of May et al.<sup>14</sup> showed agreement to within the experimental uncertainty for temperatures from 298 K to 394 K. However, at higher temperatures, it was suggested<sup>10</sup> that the use of a ground-state potential introduced a positive bias in the calculated viscosities at high temperatures, so the experimental values of Guevara were weighted more heavily than the *ab initio* calculations for temperatures above 1100 K. Finally, very recently Berg and Moldover<sup>25</sup> critically reviewed all measurements of the viscosity of 11 gases near 25 °C and zero density and provided a recommended value for calibration purposes for normal hydrogen that we have incorporated in the zero-density correlation.

For primary data for the development of the excess contribution, we selected the data of Diller,<sup>17</sup> Golubev and Petrov,<sup>26</sup> Hurly,<sup>15</sup> Johns,<sup>27</sup> Kuss,<sup>28</sup> May et al.,<sup>14</sup> Mehl et al.,<sup>10</sup> Michels et al.,<sup>22</sup> Nabizadeh et al.,<sup>12</sup> Rudenko and Slyusar,<sup>29</sup> and Tsederberg,<sup>30</sup> and Yusibani et al.<sup>16</sup> Only data at temperatures greater than 150 K were selected from Rudenko and Slyusar.<sup>29</sup> The data of Rudenko and Slyusar<sup>29</sup> display considerable scatter, but it was necessary to include at least some of this data set since they provide the only high-pressure data at temperatures between 150 K and 298 K. Preliminary work indicated that it was not possible to fit both the Rudenko and Slyusar data over the temperature range 33 K to 150 K at pressures to 70 MPa and the data of Diller over the temperature range 33 K to 100 K at pressures to 35 MPa to within their estimated uncertainties, so we selected only the Diller data for this temperature and pressure range. We also excluded from consideration as primary any data of Diller at isotherms near critical. We then subtracted

# Table 5. Summary of Results<sup>*a*</sup>

first author	no. pts.	T range/K	p range/MPa	est. unc./%	AAD	bias	RMS
Breitenbach <sup>32</sup>	5	252 to 575	0.1	na	2.1	<i>−</i> 1.7̀	1.4
Markowski <sup>33</sup>	3	287.6 to 457.3	0.1	na	1.0	-1.0	0.1
Schmitt <sup>34</sup>	10	78.3 to 458.4	0.1	na	1.6	-1.6	2.2
Kamerlingh Onnes <sup>35</sup>	17	20 to 294	0.03 to 0.06	2	4.3	-4.2	3.9
Vogel <sup>36</sup>	7	21 to 273.1	0.01 to 0.1	na	5.4	1.3	7.0
Gille <sup>37</sup>	7	273 to 373	0.1	na	0.7	-0.7	0.3
Verschaffelt <sup>38</sup>	1	20.35	0.1	1	17.5	17.5	na
Yen <sup>39</sup>	1	296.1	0.1	na	0.4	0.4	0.0
Gunther <sup>40</sup>	8	15 to 273	0.01 to 0.1	na	13.8	11.2	14.3
Ishida <sup>41</sup>	1	321	0.1	0.3	0.7	0.7	na
Klemenc <sup>42</sup>	1	273	0.1	na	1.4	-1.4	na
Gunther <sup>+3</sup>	16	15 to 273	0.01 to 0.1	na	13.0	10.4	13.5
Trautz <sup>45</sup>	12	195.2 to 523.2	0.1	na	1.3	0.7	1.4
Trautz <sup>46</sup>	20	288.6 to 523.6	0.1	na	1.2	1.2	1.6
Trautz <sup>10</sup>	15	192.4 to 524.9	0.1	na	1.1	0.9	0.8
Boyd <sup>17</sup>	56	303 to 343	7.2 to 19.4	na	6.7	-6.1	5.3
1 rautz Transta <sup>49</sup>	6	298.2 to 523.2	0.1	na	0.8	0.8	0.4
Trautz <sup>50</sup>	8	293.1 to 523.4	0.1	na	0.9	0.6	0.8
Trautz	8	289.8 to 1099.0	0.1	na	2.2	2.2	1.2
Trautz <sup>52</sup>	12	$295.2 \ 10 \ 525.4$	0.1	na	0.9	0.9	0.5
Trautz <sup>53</sup>	12	300.0  to  331.2	0.1	na	0.9	0.9	0.5
Sutherland <sup>54</sup>	12	74.8 to 293.8	0.1	11a 0.4	0.8	-0.1	0.4
Gibson <sup>55</sup>	20	74.8 10 295.8	1.1 to 29.9	0.4	0.7	-0.1	0.0
Trautz <sup>56</sup>	4	293 to 523	0.1	na	0.9	0.9	0.4
Trautz <sup>57</sup>	1	90	0.1	na	2.7	2.7	na
van Cleave <sup>58</sup>	1	295	0.1	0.2	0.5	0.5	na
Adzumi <sup>59</sup>	9	293 to 373	0.1	na	4.7	-4.7	0.1
Keesom <sup>60</sup>	14	14.5 to 20.3	0.01 to 0.1	2	25.0	-25.0	2.5
van Itterbeek <sup>61,62</sup>	11	14 to 292.9	0 to 0.01	na	6.2	-6.2	4.1
Johns <sup>27</sup>	42	14.3 to 20.7	0.15 to 0.28	1.1	1.5	-1.1	1.4
Johnston <sup>63</sup>	24	90 to 300	0.02 to 0.1	0.3 to 0.7	0.8	-0.8	0.7
Keesom <sup>64</sup>	21	13.9 to 20.5	0.01 to 0.1	2	13.5	-13.5	1.8
van Itterbeek <sup>65</sup>	39	14.9 to 292.5	0 to 0.1	na	103.6	90.1	208.5
van Itterbeek <sup>66</sup>	6	14.9 to 291.8	0.01 to 0.1	na	7.5	-7.5	4.7
van Itterbeek <sup>67</sup>	5	14.7 to 20.4	0.01 to 0.1	na	5.8	4.1	4.5
Wobser <sup>68</sup>	5	293.1 to 371.2	0.1	na	0.3	0.3	0.2
Buddenberg <sup>69</sup>	7	293 to 301	0.1	na	0.4	0.3	0.3
Kuss <sup>28</sup>	27	298 to 348	0.1 to 49	2	0.5	0.4	0.3
Kompaneets <sup>70</sup>	7	284 to 873	0.1	na	0.9	0.3	1.1
Michels <sup>22</sup>	95	298.1 to 398.1	2.6 to 186.3	0.2	0.3	-0.2	0.3
Kestin <sup>71</sup>	1	294	0.1	0.2	0.3	-0.3	na
Rietveld <sup>72</sup>	7	14.4 to 293.1	0 to 0.004	na	4.5	-4.1	5.0
Coremans <sup>73</sup>	14	20 to 78	0.1	2	3.6	-3.6	1.5
Kestin <sup>75</sup>	10	298	0.1 to 7.1	0.2	0.5	-0.5	0.2
Kestin <sup>75</sup>	9	293	0.4 to 8.4	0.05	0.9	-0.9	0.1
Rietveld <sup>70</sup>	14	14.4 to 293.1	0.0005 to 0.005	3	5.5	-5.5	6.9
Kestin <sup>77</sup>	13	293 to 303	0.1 to 0.6	0.2	0.4	-0.4	0.0
Rudenko Dama <sup>79</sup>	8	14.5 to 20.4	0.01 to 0.1	1.3	/.1	/.1	0.7
Darua Dillor <sup>17</sup>	38	223 to 423	0.8 to 15.0	0.2	0.3	-0.1	0.4
Diller <sup>17</sup> **	13	14 to 20	Sat inquid 0.04 to $21.7$	0.5	0.7	-0.0	6.0
Menabde <sup>80</sup>	320 11	77 4 to 200 6	0.006	2	2.2 17	-0.0	0.0
Tsederberg <sup>30</sup>	28	288 6 to 900 4	4.4 to 50.6	3	1.7	1.7	10
Golubev <sup>81</sup>	20 96	200.0 10 990.4 77 to 273	0.9 to 49.1	5	2.2	1.5 2.1	20
Andreev <sup>82</sup>	11	2.93	0.1 to 49	1.5	0.5	-0.4	0.4
Konareeva <sup>83</sup>	10	14 to 32	0 to 1	1.5	5.0	3.7	4.0
Kestin <sup>84</sup>	13	293 to 303	0 to 2.4	0.2	0.4	-0.4	0.1
Rudenko <sup>85</sup>	91	33.2 to 300	0.1 to 217.1	1.5	7.8	-7.1	9.2
Gracki <sup>86</sup>	42	173 to 298	0.4 to 17.1	0.2	0.3	-0.1	0.3
Guevara <sup>23</sup>	23	1103 to 2152	0.1	$2^{\dagger}$	1.1	1.1	0.3

Table 5. continue
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first author	no. pts.	T range/K	p range/MPa	est. unc./%	AAD	bias	RMS
Golubev <sup>87</sup>	58	298 to 523	0.1 to 81.6	na	0.7	0.3	0.8
Kestin <sup>88</sup>	3	295 to 308	0.1	0.1	0.1	-0.1	0.1
Carey <sup>89</sup>	18	291 to 299	0.15 to 11	0.1	0.5	0.1	0.5
Chuang <sup>90</sup>	37	173 to 273	0.4 to 50.6	0.5	0.7	0.7	0.8
Clifford <sup>21</sup>	2	298 to 308	0.1	0.2	0.2	-0.2	0.0
Lukin <sup>91</sup>	23	76.5 to 293.2	0.1	0.3	1.4	-1.4	1.0
Nabizadeh <sup>12</sup>	76	295.6 to 399.2	0.1 to 5.8	0.5 to 1	0.9	-0.9	0.7
Maltsev <sup>13</sup>	3	500 to 1100	0.3	3	1.4	-1.4	0.3
May <sup>14</sup>	32	213.6 to 394.2	0 to 0.11	0.08	0.1	0.0	0.1
Mehl <sup>10</sup>	20	20 to 2000	0	0.08 to 10	0.5	-0.5	0.7
Hurly <sup>15</sup>	111	225 to 400	0.3 to 3.4	0.5	0.3	-0.2	0.3
Yusibani <sup>16</sup>	17	294 to 400	4.6 to 99.3	2	1.6	0.3	1.7

<sup>*a*</sup>Abbreviations: est. unc., estimated uncertainty; no. pts., number of points; na, not available; AAD, absolute average percent deviation; bias, average percent deviation; RMS, root mean square. Values in bold type are considered primary data. Double asterisk (\*\*) = parahydrogen.



Figure 5. Comparison against the primary data set of the present model as a function of temperature for pressures up to 200 MPa.



**Figure 6.** Comparison against the primary data set of the present model as a function of pressure for temperatures between 200 K and 400 K.

off the dilute contribution to obtain the excess viscosity. Any data points that resulted in a negative value of the excess viscosity were also excluded from the primary data set. The resulting primary set for the excess viscosity covers the temperature range 14 K to 2000 K at pressures up to 217





MPa. Finally, we note that temperatures for all data were converted to the ITS-90 temperature scale<sup>31</sup> and the equation of state of Leachman et al.<sup>18</sup> was used to provide the density for each experimental state point. The uncertainty in density calculated from this equation of state is estimated to be 0.1 % at temperatures from the triple point to 250 K and at pressures up to 40 MPa, except in the critical region, where uncertainties are larger. In the region between 250 K and 450 K and at pressures to 300 MPa, the uncertainty in density is 0.04 %, while at temperatures between 450 K and 1000 K, the uncertainty in density increases to 1 %.



Figure 8. Comparison against the primary data set as a function of pressure for three correlations.

**Zero-Density Limit.** The zero-density limit of the viscosity  $\eta_0$  (*T*) may be approximated by the expression<sup>5</sup>

$$\eta_0(T) = \frac{0.021357(MT)^{0.5}}{\sigma^2 \mathcal{S}^*(T^*)}$$
(3)

where  $S^*$  is a reduced effective cross section, M = 2.01588 is the molar mass in g·mol<sup>-1</sup>,  $\sigma$  is a length scaling parameter in nm,  $\eta_0$  is in  $\mu$ Pa·s, and the temperature *T* is in K. It is common to express the effective cross section with the functional form<sup>5</sup>

$$\ln(\mathcal{S}^*(T^*)) = \sum_{i=0}^{4} a_i (\ln(T^*))^i$$
(4)

where the reduced temperature is  $T^* = k_{\rm B}T/\varepsilon$  and  $\varepsilon/k_{\rm B}$  is an energy scaling parameter in K. For the scaling parameters  $\sigma$  and  $\varepsilon/k_{\rm B}$  we adopt the same values used by Behnejad and Miralinaghi,<sup>92</sup> namely  $\sigma = 0.297$  nm and  $\varepsilon/k_{\rm B} = 30.41$  K. We then fit the primary experimental data for the dilute gas<sup>10,14,23</sup> with the ODRPACK orthogonal distance regression package93 and weighting factors of the square of the inverse of the experimental uncertainty for all points except the lowtemperature (T < 100 K) values of Mehl et al.<sup>10</sup> that were given increased weights in order to have the final representation be within 1 %. In addition, we constrained the fit to agree with the recommended zero-density value of Berg and Moldover<sup>25</sup> at 25 °C, 8.8997  $\mu$ Pa·s. The final values of the coefficients are given in Table 2. Deviations of the primary data and the correlation given by eq 3 and 4 are shown in Figure 3. Also shown are deviations from secondary data sets measured after 1950. The dilute-gas expression given by eq 3 and eq 4 with the coefficients in Table 2 represents the experimental data sets of May et al.<sup>14</sup> and Guevara et al.<sup>23</sup> to within their ascribed experimental uncertainty, and the theoretical values of Mehl et al.<sup>10</sup> to within 1 % for temperatures less than 1000 K. The deviations from Mehl et al.<sup>10</sup> increase at higher temperatures to 3 % at 2000 K. As mentioned earlier, we have chosen the experimental values of Guevara et al.<sup>23</sup> over the *ab initio* calculations for the highest temperatures.

There are several correlations for the zero-density viscosity of hydrogen<sup>3,16,20,94</sup> with which comparisons can be made; these are shown in Figure 4. We include the correlation of McCarty<sup>94</sup> that, although unpublished in the literature, has been adopted as the default model in the REFPROP<sup>95</sup> software package. The high-temperature values of the zero-density correlation of McCarty<sup>94</sup> are based on a modified Enskog model of Hanley et al.96 that incorporates a Lennard-Jones 12-6 potential with quantum-mechanical collision integrals for parahydrogen for the dilute gas; we were unable to ascertain the basis of the hightemperature behavior of the Vargaftik et al.<sup>3</sup> correlation. At high temperatures, the present correlation agrees well with the correlation of Assael et al.<sup>20</sup> and that of Yusibani et al.,<sup>16</sup> due in part to the selection of the Guevara et al.<sup>23</sup> data set as primary. The low-temperature behavior of the present correlation is based on the *ab initio* calculations of Mehl et al.<sup>10</sup> and the highly accurate recent data of May et al.<sup>14</sup> that were unavailable to some of the earlier researchers. The Yusibani et al.<sup>16</sup> correlation is valid for 40 K < T < 2130 K, and is in good agreement with our results.

**The Excess Contribution.** The excess contribution, eq 2, represents the behavior of the viscosity outside of the critical region as a function of both density and temperature. The initial-density coefficient of the viscosity  $\eta_1(T)$  may be written<sup>5</sup>

$$\eta_1(T) = B_\eta(T)\eta_0(T) \tag{5}$$

where  $B\eta(T)$  is the second viscosity virial coefficient and  $\eta_0(T)$  is the zero-density contribution from eqs 3 and 4. When sufficient high-quality, low-density data are available, such as for water,<sup>97</sup> the initial density dependence may be obtained directly from experimental data. Rainwater and Friend<sup>11,98</sup> developed a theoretical representation of  $B\eta$  that later was expanded upon by Vogel and co-workers.<sup>5,99</sup> More recently, Behnejad and Miralinaghi<sup>92</sup> used the Rainwater—Friend theory to develop an expression for the second viscosity virial coefficient of hydrogen that we adopt in this work:

$$B_{\eta}^{*}(T^{*}) = B_{\eta}/\sigma^{3} \tag{6}$$

$$B_{\eta}^{*}(T^{*}) = \sum_{i=0}^{6} b_{i}(T^{*})^{-1}$$
(7)

where  $T^*$ ,  $\sigma$  are as defined earlier and the coefficients are presented in Table 3.

Little theoretical guidance exists for the determination of the term  $\Delta \eta_{\rm h}(\rho,T)$  in eq 2, so we explore the use of symbolic regression to determine both the coefficients and the functional form of this contribution.

**Symbolic Regression.** We employed the technique of symbolic regression  $(SR)^{4,100,101}$  in our effort to find a new viscosity correlation for normal hydrogen. Shokir and Dmour<sup>102</sup> demonstrated the use of a form of symbolic regression to obtain a correlation for the viscosity of pure hydrocarbons and hydrocarbon gas mixtures. Symbolic regression is a specific application of genetic programming (GP) that allows one to explore arbitrary functional forms in

order to fit data. These functional forms are constructed by using a set of operators, parameters, and variables as building blocks for functions of arbitrary complexity. Using a classic GP algorithm for this function search is very slow and, even for relatively simple data fitting problems, requires many days of computing on current computing hardware. An improved GP algorithm based on multiobjective optimization and preferential evolution of models near the Pareto front has recently been developed<sup>103</sup> that greatly improves the efficiency of the search and brings it into the realm of current, desktop computer technology. This method addresses many of the numerous problems associated with SR including the issues of runaway complexity, evolutionary lock-in, and slow model development. There are two available software realizations of SR<sup>104,105</sup> that use similar overall architecture, but vary in the details of the algorithm implementation. (Certain trade names and company names are mentioned to specify adequately the materials used. In no case does such identification imply endorsement by NIST, nor does it imply that the materials are the best.) However, both packages produce a similar result after optimization, which is a set of functions that are ranked by a combination of complexity and quality of data fit. We have found that using both packages allows us to increase the diversity of models suggested by SR and, therefore, gives us a better pool of results from which to choose. Our experience indicates that some criteria necessary for a good viscosity data correlation are very difficult to automatically enforce in SR and must be enforced during the postoptimization model selection process. These criteria include reasonable extrapolation behavior and exclusion of functions that produce nonphysical results such as negative viscosities or infinite viscosities.

Our specific choice of model search for the viscosity of hydrogen was the following. We initialized SR optimization with the set of operators  $\{+,-,*,/,Exp,\wedge\}$  and the operands  $\{constant,T,\rho\}$  to simultaneously optimize function complexity and mean absolute error. Initial weights based on the estimated uncertainty of the data were also utilized. The form optimized was

$$f(T, \rho) = \eta(T, \rho) - \eta_0(T) - \eta_1(T)\rho$$
(8)

where  $\eta_0$  is obtained from eqs 3 and 4 and  $\eta_1$  is from eqs 5 to 7. Several hundred individual evolutions that each typically involved  $\sim 10^{11}$  function evaluations and 100 h of c.p.u. core time were performed to identify an optimal function that is both relatively simple and able to fit the data well. Some terms appeared repeatedly; one was a scaled density, in this case 0.011 $\rho$  (where  $\rho$  has units of kg·m<sup>-3</sup>), or equivalently  $\rho$ /90.5. Therefore, we made additional runs where the density and temperature were both scaled, with  $T_r = T/T_c$  and  $\rho_r = \rho/\rho_{sc}$ . For temperature, we scaled with the critical temperature 33.145 K;<sup>18</sup> for density we used the scaling factor  $\rho_{sc} = 90.5 \text{ kg} \cdot \text{m}^{-3}$ . This value is interesting in that it is a very compressed liquid state, close to the value of the density of the liquid at the triple point (77.00 kg·m<sup>-3</sup>). In 1971, Hildebrand<sup>106</sup> modified the earlier work of Batschinski<sup>107</sup> and introduced the concept of an intrinsic volume where the fluidity is zero. Since then, various researchers<sup>5,108-110</sup> have successfully used variations of this concept to model the viscosity of a range of fluids, and it is interesting that symbolic regression suggests a scaling in terms of a very compressed-state density. Future work will investigate if this same type of term arises for other fluids.

The final choice of model function was done in an *ad hoc* fashion after reviewing the overall fits to data, the extrapolation

behavior and the relative simplicity of numerous models. Finally, the constant elements of the model were reoptimized using a differential evolution nonlinear fitting algorithm to produce the final functional form:

$$\eta(T, \rho) = \eta_0(T) + \eta_1(T)\rho + c_1\rho_r^2 \times \exp\left[c_2T_r + c_3/T_r + \frac{c_4\rho_r^2}{c_5 + T_r} + c_6\rho_r^6\right]$$
(9)

In this equation  $\eta_0(T)$  is obtained from eqs 3 and 4,  $\eta_1(T,\rho)$  from eqs 5 to 7, the scaled temperature is  $T_r = T/T_c$  and the scaled density  $\rho_r = \rho/\rho_{\rm sc}$  where the temperature is expressed in Kelvin, densities in kg·m<sup>-3</sup>, and the viscosity  $\eta$  is expressed in  $\mu$ Pa·s. The quantity  $\rho_{\rm sc}$  is a compressed-state density used for scaling that the symbolic regression procedure identified as 90.5 kg·m<sup>-3</sup>.

Comparison with Experimental Data and Previous **Correlations.** Comparisons with the experimental data are presented in Table 5, which gives the number of data points, the original authors' estimated uncertainty of the data, average percent deviation, average absolute percent deviation, and a root-mean-square error of each data source. We define the percent deviation as  $P = 100 \times (\eta_{exp} - \eta_{calc})/\eta_{exp}$ , where  $\eta_{exp}$  is the experimental value of the viscosity and  $\eta_{\rm calc}$  is the value calculated from the present correlation. The average absolute percent deviation (AAD) is found with the expression AAD =  $(\sum |P|)/n$ , where the summation is over all *n* points; the average percent deviation (bias) is AVG =  $(\sum P)/n$ , and the we use RMS =  $([n\sum P^2 - (\sum P)^2]/n^2)^{1/2}$ . Table 5 summarizes the performance of the new model. Figures 5 and 6 show comparisons with the primary data for normal hydrogen over the temperature range 200 K to 400 K at pressures to 200 MPa; the agreement is to within about 4 %. For the region between 200 K and 400 K at pressures up to atmospheric, the present correlation reproduces the high-accuracy data of May et al.<sup>14</sup> to within 0.1 %. In Figures 7 and 8 we compare the performance of the correlation given by eqs 2 and 3, eqs 5 to 7, and eq 9 against that of the correlation of Vargaftik et al.,<sup>3</sup> and that of the McCarty model, as implemented in the NIST Standard Reference Database 23 (REFPROP).<sup>95</sup> As mentioned earlier, the default correlation in v9.0 and earlier of REFPROP is based on the unpublished work of McCarty;94 this model relied heavily on the data of Diller.<sup>17</sup> The recently developed model of Yusibani et al.<sup>16</sup> is not included in the comparisons because it is limited to temperatures above 40 K for the dilute gas and above 100 K for pressures up to 220 MPa. As shown in Figures 7 and 8, the SR correlation performs comparably to the Vargaftik<sup>3</sup> and McCarty<sup>94,95</sup> correlations. The largest deviations shown in Figures 7 and 8 for the SR correlation are for parahydrogen data of Diller<sup>17</sup> as the critical region is approached. There are few liquid-phase data available, but comparisons with the data of Johns<sup>27</sup> and the saturated liquid data of Diller<sup>17</sup> indicate agreement with the data to within 4 %. The McCarty model was not developed for pressures above 100 MPa, and this is evident from Figure 8.

### CONCLUSION

A new wide-ranging correlation for the viscosity of normal hydrogen was developed by way of a symbolic regression methodology. The correlation covers the temperature range from the triple point to 1000 K and pressures up to 200 MPa and extrapolates in a physically reasonable manner to 2000 K. The dilute-gas viscosity agrees to within the experimental uncertainty of the most accurate gas phase data of May et al.<sup>14</sup> over the temperature range 213–394 K at pressures to 0.11 MPa, and also reproduces the recommended value of Berg and Moldover<sup>25</sup> at 25 °C and zero density. Outside of that region, the estimated uncertainty is 4 % for the saturated liquid and supercritical fluid phases, except along the saturated liquid boundary above 31 K and in the near-critical region, where the uncertainty is larger. The simplicity of this new correlation makes it easy to implement and demonstrates the power of symbolic regression in finding relatively simple functional forms for data correlation.

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#### Notes

The authors declare no competing financial interest.

#### ACKNOWLEDGMENTS

We thank Mark Kotanchek and Katya Vladislavleva of Evolved Analytics, LLC, for their encouragement and expertise in the use of the symbolic regression method.

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