# SELF-DIFFUSION COEFFICIENT AND VISCOSITY OF SUPERCRITICAL FLUIDS

**M. S. ZABALOY*[1], V. R. VASQUEZ[2], E. A. MACEDO[3]**

[1]Planta Piloto de Ingeniería Química, Universidad Nacional del Sur - CC 717, 8000 Bahía Blanca, ARGENTINA. E-mail: mzabaloy@plapiqui.edu.ar. Fax 54-291-486-1600. [2]Mail Stop 170, Chemical Engineering Department, University of Nevada-Reno,1664 N. Virginia St., Reno, NV 89557-0136, USA. [3]Departamento de Engenharia Química, Faculdade de Engenharia da Universidade do Porto. Rua do Dr. Roberto Frias, 4200-465 Porto, PORTUGAL

## ABSTRACT

In this work, we propose a model for representing both the viscosity and the self diffusion coefficient (SDC) of supercritical pure fluids in wide ranges of conditions. A given pure real fluid is represented as a Lennard-Jones (LJ) fluid having efective values of the LJ intermolecular potential parameters. The model is able to represent the pure compound viscosity an self diffusion coefficient of real supercritical fluids, in wide ranges of conditions, with average absolute-value relative deviations less than or about 10 % for both properties.

Key words**:** self diffusion coefficient, viscosity, supercritical real fluids, model, molecular simulation

## INTRODUCTION

The increasing interest on the use of supercritical fluids requires reliable models for their thermophysical properties. Such models should preferably make reference to some adopted form for the intermolecular potential function. Models for viscosity are required for, e.g., the calculation of mass transfer coefficients. Models for the self diffusion coefficient are required for models of the tracer diffusion coefficient [1], which also influences the mass transfer coefficient. In this work, we concentrate on modeling the viscosity and the self diffusion coefficient (SDC) of pure real fluids at temperatures and pressures beyond their critical values, i.e., at supercritical conditions. The model is based on the Lennard-Jones (LJ) fluid transport and thermodynamic properties.

## THE LENNARD-JONES(LJ) FLUID

The expression for the Lennard-Jones (LJ) intermolecular potential is the following.

$$u(r) = 4e\left[(s/r)^{12} - (s/r)^{6}\right] \qquad (1)$$

where $r$ is the intermolecular distance, $u$ is the potential energy, $e$ is the depth of the LJ potential well, and $s$ is the LJ separation distance at zero energy. The LJ fluid is simple but realistic [2]. The LJ reduced temperature $T^+$, reduced pressure $P^+$, reduced density $r^+$, reduced SDC $D^+$ and reduced viscosity $h^+$ are conventionally defined as follows:

$$T^+ = \frac{kT}{e} \quad (2) \qquad P^+ = \frac{Ps^3}{e} \quad (3) \qquad r^+ = \frac{N}{V} s^3 = N_A\, r\, s^3 \quad (4)$$

$$D^+ = D\frac{\sqrt{m/e}}{s} \quad (5) \qquad h^+ = h\frac{s^2}{\sqrt{me}} \quad (6)$$

where $k$ is the Boltzmann constant, $T$ is the absolute temperature, $P$ is the absolute pressure, $N$ is the number of molecules, $V$ is the system volume, $N_A$ is Avogadro's number, $r$ is the mole density in units such as moles per liter, $D$ is the self-diffusion coefficient (SDC), $h$ is the Newtonian shear viscosity, and $m$ is the mass of one molecule. For the relationship among the SDC, the temperature and the density for the LJ fluid we used the following equation

$$D^+ r^+ = \left(D^+ r^+\right)_0 + \sum_{i=1}^{4} \sum_{j=1}^{6} c_{ji} \frac{\left(r^+\right)^i}{\left(T^+\right)^{(j-1)}} \tag{7}$$

where $\left(D^+ r^+\right)_0$ is the limit of the product $\left(D^+ r^+\right)$ as the density approaches zero and the coefficients $c_{ji}$ are fitting parameters. We fitted the $c_{ji}$ parameters by forcing a good reproduction of Meier’s [3] LJ self-diffusion data. For the term $\left(D^+ r^+\right)_0$ we used Eq. (B.1) of page 193 of Meier’s [3] Ph. D. thesis, rewritten in terms of dimensionless variables. Such equation has the range of applicability: from $T^+ = 0.7$ to $T^+ = 1000$. The range of applicability of Eq. (7) is, for the density, from zero to $r^+_{\mathrm{fluid},SFE}$ ( $r^+_{\mathrm{fluid},SFE}$ = density of the dense LJ fluid in equilibrium with the LJ solid ), and from $T^+ = 0.7$ to $T^+ = 6$. Zabaloy et al.[2] presented an iterative procedure to compute $r^+_{\mathrm{fluid},SFE}$ . For the relationship between viscosity, temperature and density for the LJ fluid we used the following equation

$$h^+ = h_0^+ + \sum_i \sum_j b_{ji} \frac{\left(r^+\right)^i}{\left(T^+\right)^{(j-1)}} \tag{8}$$

where $h_0^+$ is the LJ reduced viscosity limit at zero density. We fitted the $b_{ji}$ coefficients by imposing a good reproduction of the Rowley and Painter (RP) [4] LJ data ( $0.8 \le T_+ \le 4$ ), after excluding data corresponding to a metastable condition. For $h_0^+$ we used the Chapman-Enskog equation coupled to the Neufeld-Janzen-Aziz expression for the collision integral, as presented in equations (9-3.9) and (9-4.3) of reference [5], which are applicable within the wide range $0.3 \le T^+ \le 100$. We do not report here the values of the $b_{ji}$ and $c_{ji}$ coefficients due to space limitations. For the PVT LJ relationship we used the PVE/hBH LJ equation of state (EOS) [6], which we combine here with Eqs. (7) and (8) to calculate SDCs and viscosities at given temperature and pressure. The PVE/hBH LJ-EOS [6] is the following

$$z = P^+ / r^+ T^+ = f_{KN}\left(r^+, T^+\right) \tag{9}$$

where $z$ is the compressibility factor and $f_{KN}$ is a function of $r^+$ and $T^+$ available in the original reference [6] and more concisely in reference [2]. The temperature range of applicability of Eq. (9) is $0.68 \le T^+ \le 10$. The range for $r^+$ is from 0 (zero) to $r^+_{\mathrm{fluid},SFE}$ . Eq. (9) is a classical LJ EOS [6]. This is not problematic due to small critical enhancement for viscosity. The critical coordinates corresponding to Eq. (9) are the following [6]:

$T_c^+ = 1.3396$ (10) $P_c^+ = 0.1405$ (11) $r_c^+ = 0.3108$ (12)

The value of $T_c^+$ implies that Eqs. (7) to (9) cover the supercritical range. In this work, which is limited to temperatures such that $T^+ \ge T_c^+$ , the computed $r^+$ values where always less than $r^+_{\mathrm{fluid},SFE}$ . On the other hand the $T^+$ range of Eqs. (7) to (9) was never exceeded. For known values of $m, e$ and $s$ the SDC $D$ and the viscosity $h$ at given temperature $T$ and pressure $P$ are calculated as follows. (a) Calculate $T^+$ [Eq. (2)] and $P^+$ [Eq. (3)]. (b) Calculate $r^+$ using

Eq. (9). (c) Calculate $h^+$ using Eq. (8). (d) Calculate $h$ from Eq. (6). (e) Calculate $D^+$ from Eq. (7). Calculate $D$ from Eq. (5). Viscosity diverges at the critical point [2]. Eq. (8) does not account for the critical enhancement for viscosity that takes place in the neighborhood of the critical point. In contrast with the case of the thermal conductivity, the critical enhancement in viscosity is small and becomes important only within a narrow region around the critical point [2]. Therefore, it is not accounted for in this work. On the other hand no anomaly ([7],[8]) in the vicinity of the critical point exists for the SDC of real fluids. For the self-diffusion coefficient of the LJ fluid, Meier [3] did not report any critical anomaly either. Consistently, Eq. (7) does not account for any SDC critical enhancement effect. Eqs. (7) to (9), which apply to the LJ fluid, interrelate sets of dimensionless variables. The LJ fluid is therefore a corresponding states fluid where the dimensionless variables have, as a distinguishing feature, a dependency on parameters meaningful at molecular level.

## PARAMETERS

Zabaloy et al. [2] used constant values for the parameters $e$ and $s$ consistent with the experimental critical $T$ and $P$ coordinates of the pure real fluid. In this work, we define $s_c$ as the value of $s$ computed as in reference [2]. The model in ref. [2] is purely predictive. Somehow following ref. [9], we achieve here a better quantitative performance for real fluids whose molecules are polar and/or non spherical, by making $s$ temperature dependent:

$$a_s = s / s_c = 1 + s_s \left(T_r - 1\right) \qquad (13)$$

where $T_r$ is the practical reduced temperature, defined as $T_r = T/T_c$. The use of temperature dependent LJ parameters is valid for engineering purposes [10]. Eq. (13) keeps the consistency with the experimental critical $T$, $P$ coordinates. We adjusted the slope $s_s$ to match either experimental SDCs or experimental viscosities. On the other hand, we kept $e$ constant, i.e., equal to its critical value, at all temperatures. To make the model more flexible we introduce now a second adjustable parameter for each property ($F_D$ and $F_h$), which we define as follows:

$$D = F_D D^+ \frac{s}{\sqrt{m/e}} \qquad (14) \qquad\qquad h = F_h h^+ \sqrt{me} \big/ s^2 \qquad (15)$$

From the practical point of view, parameters $F_D$ and $F_h$ have, respectively, on the LJ SDC and viscosity a role analogous to parameter $A_D$ on the LJ SDC in reference [9]. The parameter $A_D$ [9] is the translational-rotational coupling factor which accounts for the non spherical nature of real fluid molecules.

## RESULTS AND DISCUSSION

Table 1 shows results for the LJ based modeling of the self diffusion coefficient (SDC) and the viscosity (VSC) of supercritical real pure fluids. The meanings of the variables in Table 1 are the following: NEDP = Number of experimental data points, AAD% = Average absolute-value percentage relative deviation [2], Max AD% = Maximum absolute-value percentage relative deviation [2] and $Pr$ = practical reduced pressure = $P/P_c$. Table 1 also shows, for every pure compound, details about the two databases we used in this work, i.e., the temperature and pressure ranges, the number of experimental data and the literature sources. The total number of experimental data points is 511 for SDC and 2614 for viscosity. Notice, for some compounds, the very high values of the maximum reduced pressure. The "Predictions" columns show the AAD% and Max AD% when no adjustable parameters are used, i.e., at $F_D = 1$ and $s_s = 0$ for SDCs and at $F_h = 1$ and $s_s = 0$ for viscosities. In such a case, the only input experimental information used was the critical temperature, critical pressure and the molecular weight, which were taken from reference [11]. If we look at viscosity, from the "Predictions" *AAD%* values in Table 1, we can conclude that compounds such as Propane, Carbon Dioxide and n-Butane can be treated, within the temperature and pressure ranges of Table 1/VSC, as LJ fluids having constant effective $e$ and $s$ parameters set to reproduce the pure compound experimental critical temperature and critical pressure. A similar conclusion is valid, if we look at SDCs, for Methane and Propane within the $T$ and $P$ ranges of Table 1/SDC. For fluids such as water or Hydrogen Sulfide, the model performance when used in a purely predictive way is not acceptable from the quantitative point of view. Table 1 also shows correlation results in the last four columns. For a given transport property, we adjusted simultaneously the $F$ and $s_s$ parameters. However, in this work, we did not attempt to correlate simultaneously SDCs and viscosities. Hence, depending on the transport property considered, i.e., either the SDC or the viscosity, we obtained a different value of the slope $s_s$ through regression. The values for the slope $s_s$ corresponded always to values of $a_s$ in the order of unity (roughly in the range 0.75 to 1.2). Parameters $F_D$ and $F_h$ are normally close to unity. Correlation of SDCs resulted in the reduction of the average error to 10 % or less, with the exception of Argon for which the experimental SDC data are significantly scattered. For viscosity, the average deviation, after fitting the parameters, for all compounds except water is less than or equal to 7 %, which is within the experimental uncertainty for viscosity at high pressure.

## CONCLUSION AND FUTURE WORK

In the present work we have shown the corresponding states nature of the Lennard-Jones (LJ) fluid and have demonstrated that it is possible to represent with a good level of accuracy the self diffusion coefficient and the viscosity of pure real supercritical fluids in wide ranges of conditions, in terms of effective parameters with some meaning at molecular level. The approach uses the molecular weight, the experimental critical temperature and the experimental critical pressure as input information together with, if necessary, a couple of well-behaved parameters fitted against experimental information. The model is able to represent the pure compound viscosity an self diffusion coefficient of real supercritical fluids, in wide ranges of conditions, with average absolute-value relative deviations less than or about 10 % for both properties. A distinguishing feature of the present approach is that the density is obtained from a LJ equation of state. Hence, the present approach is somewhat more consistent that other approaches, with regard to the properties of the reference model fluid. Therefore, no compound-specific correlations are required for the density, which in this work plays the role of an intermediate variable. In the near future we will study the simultaneous correlation of self diffusion coefficients and viscosities.

## ACKNOWLEDGEMENTS

The authors are grateful to Professor Erling H. Stenby and Mr. Claus Zéberg-Mikkelsen (Technical University of Denmark) for having provided a viscosity database; to Elodie Gonon and Eliana Abreu for helping in the preparation of the final digital versions of the SDC and viscosity databases used here; and, for financial support, to the European Commission (EVIDENT project, Contract No: JOF3-CT97-0034), to Consejo Nacional de Investigaciones Científicas y Técnicas de la República Argentina, and to University of Nevada, Reno.

## REFERENCES

1. H. Liu and E. Ruckenstein Ind. Eng. Chem. Res. , 36, 5488-5500 (1997)
2. Zabaloy, M. S.; Machado, J. M. V.; Macedo, E. A. Int. J. Thermophysics, 2001, 22, 829.
3. K. Meier.Computer Simulation and Interpretation of the Transport Coefficients of the Lennard-Jones Model Fluid. Shaker Verlag, Aachen, ISBN 3-8322-0968-9 (2002).
4. R.L Rowley and M.M. Painter, Int. J. Thermophys. 18: 1109 (1997).
5. R.C. Reid, J.M. Prausnitz, B.E. Poling, The Properties of Gases & Liquids, Fourth Ed., McGraw-Hill Internat. Ed. New York (1987) pp. 392-393
6. J. Kolafa and I. Nezbeda, Fluid Phase Equilib. 100: 1 (1994).
7. H. Lee and G. Thodos. Ind. Eng. Chem. Fundam. 22, 17-26 (1983)
8. S. De, Y. Shapir, E.H. Chimowitz. Chem. Eng. Sci. 56, 5003-5010 (2001)
9. E. Ruckenstein, H. Liu, Ind. Eng. Chem. Res., 36, 3927 (1997)
10. T. Sun and A.S. Teja, Ind. Eng. Chem. Res. 37: 3151 (1998).
11. DIPPR 801, Evaluated Process Design Data, Public Release (1998), American Institute of Chemical Engineers, Design Institute for Physical Property Data, BYU-DIPPR, Thermophysical Properties Laboratory. Provo, Utah.
12. Dawson, R., Khoury, F. and Kobayashi, R. A.I.Ch.E.J. 16, 725. (1970)
13. Harris, K. R. Physica 94A, 448.(1978)
14. G.-Schmid, A., Wappmann, S., Has, M. and Ludemann, H.-D. J. Chem. Phys. 94, 5643.(1991)
15. Takahashi, S.J. Chem. Engng Japan 10, 339.(1977)
16. Arends, B., Prins, K. O. and Trappeniers, N. J. Physica 107A, 307. (1981)
17. 0'Hern, H. and Martin J. J. Ind. Engng Chem. 47, 2081.(1955)
18. Takahashi, S. and Iwasaki, H. Bull. Chem. Soc. Japan 39, 2105.(1996)
19. Etesse, P., Zega, J. A. and Kobayashi, R. J. Chem. Phys. 97, 2022.(1992)
20. Mifflin, T. R. and Bennett, C. O. J. Chem. Phys. 29, 975 (1958)
21. Carelli, P., Modena, I. And Ricci, F. P. Phys. Rev. A 7, 298. (1973)
22. Carelli, P., De Santis, A., Modena, I. And Ricci, F. P. Phys. Rev. A 13, 1131. (1976)
23. Prielmeier, F. X. and Ludemann, H.-D. Mol. Phys. 58, 593.(1986)
24. Harris, K. R. Physica 93A, 593. (1978)
25. Has, M. and Ludemann, H.-D. Naturf. 44a, 1210.(1989)
26. Khoury, F. and Kobayashi, R. J. Chem. Phys. 55, 2439.(1971)
27. Lamb, W. J., Hoffman, G. A. and Jonas,J. Chem. Phys. 74, 6875 (1981)
28. Finney, R. J., Fury, M. and Jonas, J. J. Chem. Phys. 66, 760.(1977)
29. K. Stephan and K. Lucas, *Viscosity of Dense Fluids* (Plenum Press, New York and London, 1979).
30. H. Gonzalez and A.L. Lee. J. Chem. Eng. Data, 13, 66 (1968)
31. Vargaftik N.B. Tables on the termophysical properties of liquids and gases. Hemisphere Publishing Corporation, Washington - London, Sec. Edition (1975)
32. Monteil J.M., Lazarre F., Salvinien J. and Viallet P. Journal de Chimie Physique 66, 1673 (1969)

**Table 1**: Prediction and correlation results for the LJ based modeling of the Self Diffusion Coefficient (SDC) and viscosity (VSC) of supercritical pure fluids

| | | | | | | | | | | | Predictions | | Correlation Results | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Compound | References | NEDP | Min T / K | Max T / K | Min P / Bar | Max P / Bar | Min Tr | Max Tr | Min Pr | Max Pr | AAD% | Max AD% | $F$ | $s_s$ | AAD% | Max AD % |
| | **SDC** | **SDC** | **SDC** | **SDC** | **SDC** | **SDC** | **SDC** | **SDC** | **SDC** | **SDC** | **SDC** | **SDC** | $F_D$ | **SDC** | **SDC** | **SDC** |
| Methane | [12][13][14] | 151 | 191 | 454 | 49 | 2070 | 1.00 | 2.38 | 1.06 | 45.0 | 8 | 20 | 1.116668 | 0.035800 | 4 | 15 |
| Ethane | [14] | 20 | 319 | 454 | 250 | 2000 | 1.04 | 1.49 | 5.13 | 41.1 | 14 | 25 | 1.165750 | -0.022805 | 6 | 13 |
| Propane | [14] | 10 | 397 | 453 | 250 | 2000 | 1.07 | 1.22 | 5.89 | 47.1 | 8 | 19 | 1.057033 | -0.098453 | 7 | 13 |
| Ethylene | [15][16] | 36 | 298 | 348 | 51 | 1828 | 1.06 | 1.23 | 1.01 | 36.3 | 12 | 26 | 1.125949 | -0.026849 | 4 | 17 |
| Carbon Dioxide | [17][18][19] | 53 | 308 | 373 | 79 | 498 | 1.01 | 1.23 | 1.06 | 6.8 | 13 | 34 | 0.997532 | -0.323261 | 7 | 25 |
| Argon | [20] | 9 | 323 | 323 | 69 | 295 | 2.14 | 2.14 | 1.41 | 6.0 | 10 | 29 | 0.989022 | 0.000000 | 10 | 28 |
| Krypton | [21][22] | 27 | 210 | 274 | 57 | 113 | 1.00 | 1.31 | 1.04 | 2.0 | 10 | 21 | 0.994934 | -0.148616 | 7 | 15 |
| Chloromethane | [23] | 4 | 440 | 440 | 500 | 2000 | 1.06 | 1.06 | 7.49 | 29.9 | 10 | 22 | 0.929740 | -0.000080 | 8 | 14 |
| Chlorotrifluoromethane | [24][25] | 85 | 303 | 433 | 40 | 2000 | 1.00 | 1.43 | 1.02 | 51.7 | 16 | 69 | 0.804783 | -0.381989 | 7 | 75 |
| Carbon Tetrafluoride | [26] | 49 | 243 | 348 | 39 | 450 | 1.07 | 1.53 | 1.04 | 12.0 | 29 | 101 | 0.589235 | -0.456621 | 10 | 24 |
| Water | [27] | 33 | 673 | 973 | 221 | 1459 | 1.04 | 1.50 | 1.00 | 6.6 | 27 | 36 | 1.364777 | -0.000006 | 6 | 13 |
| Perfluorocyclobutane | [28] | 34 | 423 | 473 | 110 | 1900 | 1.09 | 1.22 | 3.96 | 68.4 | 14 | 26 | 0.857096 | -0.166111 | 2 | 21 |
| | **VSC** | **VSC** | **VSC** | **VSC** | **VSC** | **VSC** | **VSC** | **VSC** | **VSC** | **VSC** | **VSC** | **VSC** | $F_h$ | **VSC** | **VSC** | **VSC** |
| Methane | [29] | 176 | 320 | 520 | 46 | 700 | 1.68 | 2.73 | 1.00 | 15.2 | 11 | 15 | 1.0356 | -0.0443 | 2 | 6 |
| Ethane | [29] | 170 | 320 | 700 | 49 | 700 | 1.05 | 2.29 | 1.00 | 14.4 | 7 | 12 | 1.0516 | -0.0390 | 3 | 8 |
| Propane | [29] | 168 | 400 | 750 | 43 | 350 | 1.08 | 2.03 | 1.00 | 8.2 | 4 | 10 | 1.0351 | -0.0102 | 2 | 7 |
| n-Butane | [29] | 191 | 450 | 800 | 38 | 700 | 1.06 | 1.88 | 1.00 | 18.4 | 6 | 28 | 0.9321 | -0.1109 | 7 | 17 |
| n-Pentane | [29] | 160 | 490 | 850 | 34 | 500 | 1.04 | 1.81 | 1.00 | 14.8 | 9 | 18 | 1.0815 | -0.0192 | 3 | 11 |
| n-Heptane | [29] | 112 | 550 | 620 | 27 | 500 | 1.02 | 1.15 | 1.00 | 18.2 | 10 | 24 | 1.1047 | 0.0929 | 6 | 13 |
| n-Octane | [29] | 25 | 575 | 670 | 25 | 500 | 1.01 | 1.18 | 1.00 | 20.1 | 10 | 19 | 1.0680 | -0.0834 | 6 | 14 |
| iso-Butane | [29] | 254 | 420 | 850 | 37 | 500 | 1.03 | 2.08 | 1.00 | 13.7 | 7 | 24 | 1.0056 | -0.0086 | 6 | 23 |
| iso-Pentane | [29] | 143 | 470 | 750 | 40 | 600 | 1.02 | 1.63 | 1.18 | 17.8 | 15 | 28 | 1.1785 | -0.0317 | 4 | 15 |
| Neopentane | [30] | 9 | 444 | 444 | 41 | 552 | 1.02 | 1.02 | 1.29 | 17.3 | 29 | 33 | 1.4040 | -1.3638 | 1 | 4 |
| Ethylene | [29] | 285 | 300 | 700 | 51 | 800 | 1.06 | 2.48 | 1.00 | 15.9 | 7 | 15 | 1.0600 | -0.0316 | 4 | 10 |
| Propylene | [29] | 357 | 380 | 650 | 46 | 900 | 1.04 | 1.78 | 1.00 | 19.6 | 11 | 39 | 1.1204 | 0.0143 | 4 | 31 |
| Carbon Dioxide | [29] | 347 | 310 | 900 | 74 | 1000 | 1.02 | 2.96 | 1.00 | 13.5 | 5 | 15 | 1.0285 | -0.0085 | 4 | 13 |
| Water | [31] | 184 | 653 | 973 | 230 | 800 | 1.01 | 1.50 | 1.04 | 3.6 | 18 | 33 | 1.0349 | -0.4467 | 11 | 22 |

| | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Hydrogen Sulfide | [32] | 33 | 388 | 413 | 100 | 500 | 1.04 | 1.11 | 1.12 | 5.6 | 45 | 72 | 1.8110 | 1.1616 | 6 | 27 |