# A Calculation for the Viscosity of Fluid at the Critical Point

**Wonsoo Kim[*] and Tong-Seek Chair[†]**

*Department of Metallurgical Engineering, Hongik University, Chochiwon 339-800, Korea*
*[†]Department of Chemistry, Korea University, Seoul 136-701, Korea*

*Received March 7, 2002*

It is very difficult to measure the fluid viscosity at the critical point, there are seldom found experimental values of fluid viscosity at the critical point. Few theories can explain the critical viscosity quantitatively. A theory of viscosity previously proposed by authors[10] is applied to the fluid at the critical point. This theory can be simplified as a simple form with no adjustable parameters, allowing for easy calculation. Viscosities at the critical point for some substances have been calculated, and calculated results are satisfactory when compared with the observed values.

**Key Words :** Viscosity of fluids, Viscosity at the critical point, Theory of viscosity

## Introduction

Gas phase viscosity is primarily a function of momentum transfer by translation of the molecules with relatively few collisions and has been described by kinetic theory of gases. In dense gases and liquids, however, the monentum transfer is dominated by collisions and interacting force fields between the densely packed molecules. The theoritical description of dense gases and liquids is difficult due to these intermolecular forces, which consists of short range effects such as repulsions and hydrogen bonding, wide range effects such as electrostatic effects and long range effects such as attractions. Statistical mechanics represents a fundamental idea about the interaction of molecules in dense gases and liquids. However in order to predict properties like viscosity, proper distribuion functions describing the intermolecular force field or intermolecular potential energy function are needed. Those distribution function, as for instance, the Lennard-Jones potential function, require information about a characteristic collision diameter and a reference intermolecular potential of the molecule. This information is not available a priori and must be obtained by fitting experimental data. The uncertainties contained in the distribuion function transform the theoretically fundamental statistical mechanical approach into a semi-empirical method, if used in practice. The viscosity of the fluids exhibits an anomalous behavior in the vicinity of the critical point. The explanation for this phenomenon is not clear Owing to the difficulty of approaching very close to the critical point, only a few studies of the viscosity behavior have been reported. At the present time, the approximate theory of Enskog[1] is the most usable for describing the viscosity of real gases. Several models for predicting the viscosity for dense gases and liquids are available in an abundance of literature with excellent reviews available by Reid *et al.*,[2] Touloukian *et al.*,[3] Stephan and Lucas,[4] and Viswanath & Natarajan,[5] and no theory available can predict the viscosity for both dense gases and liquids, much less the unusual viscosity behavior around the crtitical point. Some decoupled theories[6] had been applied to the critical viscosity with little success. As a results, the only equation available[7] for the prediction of the viscosity near the critical point is empirical in nature. The empirical equation, however, was not able to provide the variables involved with a clear explanation of their physical meanings, and it seemed necessary to poropose a theoretical model that may be used near the critical point. The present authors, therefore, came to present in the previous paper[8] an equation that might give a quantitative estimation of the viscosity around the critical point. It was found that the equation could also be used to calculate the viscosity right at the critical point. Recently, it has been suecessfully applied to the liquid metals[9] for the prediction of viscosity , which is an excellent test for checking the validity of the liquid theory. This paper will use the phenomenological theory of viscosity[10] previously proposed by authors to present a viscosity equation that might be used to calculate the viscosity at the critical point.

## Theory

Let a shear stress $\alpha$ be applied with a shear rate $\kappa$ to a fluid which contains N molecules in a volume V at the temperature. If the resulting flow is a Newtonian, the shear viscosity defined by

$$\eta = \alpha/\kappa \tag{1}$$

is independent of the shear stress and the shear rate. Since the viscosity results from the kinetic molecular motions and the intermolecular interactions in the fluid, the viscosity can be expressed as

$$\eta = \eta_k + \eta_i \tag{2}$$

where $\eta_k$ and $\eta_i$ are the viscosities contributed by the kinetic molecular motions and the intermolecular interactions in the fluid, respectively. If the fluid is homogeneous with respect to the external forces, the viscosities $\eta_k$ and $\eta_i$ may be proportional to the corresponding pressure as,

$$\eta_K = \zeta_k P_k / \kappa \tag{3}$$
$$\eta_i = \zeta_i P_i / \mathrm{k} \tag{4}$$

where $P_k$, $P_i$ are the kinetic pressure and the internal pressure of the fluid respectively and $\zeta$ is the proportionality factor which may be related to the external forces. In conjunction with the shear rate, we assume that the rate is proportional to the velocity of the molecule as,

$$\kappa = \zeta V_m / \lambda \tag{5}$$

where $V_m$ and $\lambda$ are the molecular velocity and the mean free path of molecules. For the Newtonian flow, the proportionality factor $\zeta$ in Eqs. (3), (4) and (5) should be the same to have the viscosity which is independent of the external force. Therefore we can get a equation of viscosity[8] as follows.

$$\eta = (P_k + P_i)/(V_m/\lambda) \tag{6}$$

The kinetic and internal pressures are given by,

$$P_k = T(\partial P/\partial T)_v \tag{7}$$
$$P_i = (\partial E/\partial V)_T \tag{8}$$

where $T$, $P$, $E$ and $V$ are the temperature, pressure, internal energy and volume, respectively. To find out the kinetic pressure and internal pressure we need an equation of a state of the fluid. For the dense gas region including the critical point, however, it is not easy to find the appropriate equation of state. In this paper we adapt an equation derived from Roulette liquid theory[11] as follows

$$P = \mathrm{R}T/(V-b)-a/V^n \tag{9}$$

where three parameters $a$, $b$ and $n$ are estimated from the critical point and the inversion temperature.[12] This equation also should satisfy the thermodynamic stability criteria at the critical point,

$$(\partial P/\partial V)_{Tc} = 0 \tag{10}$$
$$(\partial^2 P/\partial V^2)_{Tc} = 0 \tag{11}$$

where $T_c$ is the temperature at the critical point.

If Eq. (9) is used with Eq. (10) and Eq. (11), it is readily shown that

$$n = 2Z_c + (4Z_c^2 + 1)^{1/2} \tag{12}$$

$$a = (n+1)P_c V_c^n/(n-1) \tag{13}$$

$$b = (n-1)V_c/(n+1) \tag{14}$$

where $Z_c$, $P_c$, and $V_c$ are the compressibility factor, the critical pressure and the critical volume, respectively. Thus, with values of critical pressure, volume and temperature for any material, $a$, $b$, and $n$ are easily determined. By using the equation (9), we have

$$P_k = \mathrm{R}T/(V-b) \tag{15}$$
$$P_i = a/V^n \tag{16}$$

In conjunction with the molecule in a gas, we have

$$\lambda = V/(2^{1/2}\pi\sigma^2 N) \tag{17}$$
$$V_m = (8\,\mathrm{k}T/(\pi m))^{1/2} \tag{18}$$

where $\sigma$, $k$ and m are the collision diameter, boltzmann constant and mass of a molecule, respectively. By introducing Eqs. (13) through (18) into Eq. (9), we can obtain the viscosity of the critical point, $\eta_c$, as follows

$$\eta_c = (n+1)\mathrm{R}T_c(0.5+Z_c/(n-1))/V_m \tag{19}$$

## Calculation Results and Discussion

To calculate the viscosity at the critical point by using Eq. (19), we take an approximation for $\sigma$ as follows

$$\sigma = \sigma_o(1+1.8\ T_b/T)^{1/2} \tag{20}$$

which is the same as the Sutherland's correction[13] equation where $T_b$ is the normal boiling point. The value of $\sigma_{o,}$, which depends upon the van der Waals constant $b$, can be obtained as follows

$$\sigma_o = (\zeta b/N)^{1/3} \tag{21}$$

where $\zeta$ is a parametric constant. In this calculation we take $\zeta$ as 0.61. The values of $V_m$, and $\lambda$ at the critical point are calculated as $73.29(n-1)V_c/((n+1)\sigma^2)$ and $145.5(T_c/M)^{1/2}$, respectively, using Eq. (12) through Eq. (16). Therefore, the equation of viscosity at the critical point can be expressed as a following form that may be used for easy calculation

$$\eta_c = 78.84(n-1)(MT_c)^{1/2}(0.5+Z_c/(n-1))/\sigma^2\ \mu\text{-poise} \tag{22}$$

, in which $M$ is molecular weight in gram, $T_c$ in $K$, and $\sigma$ in Å.

In Table 1, the calculated results of the critical point properties for some substances are shown and compared with the experimental values.

Experimental values of $\eta_c$ are seldom available. Besides, few theories have been developed for the quantitative prediction of the viscosity at the critical point. Recently, a new model[14] for predicting vapor pressure as a function of structural composition over wide temperature ranges has been proposed, but it can not predict the right shape of the viscosity curves at temperatures greater than about 0.7 times the critical temperature. Until now, $\eta_c$ has been estimated in one of the following ways; (i) if a value of viscosity is known at a given reduced pressure and temperature, preferably at condition as near to those of interest as possible, then $\eta_c = \eta/\eta_r$, where $\eta_r$ is reduced viscosity; or (ii) if only critical P-V-T data are available then $\eta_c$ by Bird[8] may

**Table 1**. Calculated critical values

| | Zc | n | $\eta_{\text{calc.}}$ $\mu$-poise | $\eta_{\text{obs.}}$ $\mu$-poise |
|---|---|---|---|---|
| Carbon dioxide | 0.27 | 1.69 | 326 | 322 |
| Ammonia | 0.24 | 1.60 | 299 | 261 |
| Methanol | 0.22 | 1.54 | 328 | 284 |
| Ethanol | 0.25 | 1.61 | 294 | 285 |
| Isopropanol | 0.25 | 1.61 | 273 | 282 |
| Isobutanol | 0.26 | 1.64 | 270 | 277 |
| Ethane | 0.29 | 1.72 | 200 | 220 |

**Table 2**. Comparison of our results with the results of Hougen and Watson

| | Our Resuts ($\mu$-poise) | Hougen and Watson[14] ($\mu$-poise) | Experiment ($\mu$-poise) |
|---|---|---|---|
| $H_2$ | 28 | 35 | – |
| He | 17 | 25 | – |
| Ne | 140 | 156 | – |
| Ar | 248 | 264 | – |
| Air | 180 | 193 | – |
| $N_2$ | 169 | 180 | – |
| $O_2$ | 226 | 250 | – |
| CO | 169 | 190 | – |
| $CO_2$ | 326 | 343 | 322 |
| NO | 300 | 258 | – |
| $N_2O$ | 325 | 332 | – |
| $SO_2$ | 396 | 411 | – |
| $Cl_2$ | 402 | 405 | – |
| $CH_4$ | 147 | 159 | – |
| $C_2H_6$ | 200 | 210 | 220 |
| Cyclohexane | 311 | 284 | – |
| $C_6H_6$ | 300 | 312 | – |
| $CH_3Cl$ | 308 | 333 | – |
| $CHCl_3$ | 372 | 410 | – |
| $CCl_4$ | 403 | 413 | – |
| $CS_2$ | 380 | 404 | – |

be estimated from

$$\eta_c = 61.6(MT_c)^{1/2}(V_c)^{-2/3} \qquad (23)$$

, in which $\eta_c$ is in micropoises, $T_c$ in $K$, and $V_c$ in cm$^3$ per gram mole. The critical viscosities computed by method(i) has been tabulated by Hougen and Watson,[15] and Table 2 reproduces the results and compares them with the values of viscosity from Eq. (22). Due to the lack of experimental data for the viscosity at the critical point, exact comparisons with experiments are difficult to be made. But the agreements between the theories and experiments turn out to be fairly good for some substances. If we sustitute 1.65 for $n$ and $0.6T_c$ for $T_b$ in Eq. (22), we can obtain a simlpe equation as follows

$$\eta_c = 58(MT_c)^{1/2}/V_c^{2/3} \qquad (24)$$

, in which $\eta_c$ is in micropoise, $T_c$ in $K$, and $V_c$ in cm$^3$ per gram mole.

This value of viscosity is expressed as a simple form similar to the empirical equation proposed by Bird[7] as

$$\eta_c = 0.98\ \eta_B \qquad (25)$$

where $\eta_B$ is the empirical viscosity at the critical point proposed by Bird.

We had sucessfully explained[8] the abnormal behavior of the viscosity near the critical point by substituting the sound velocity for the molecular velocity $V_m$ in Eq. (6). To calculate the viscosities at the critical point, we need the data for heat capacity ratio $\gamma$ around the critical point. Since we can not find the value of $\gamma$, we have to use the average speed of gas from the Maxwell distrbution for the molecular velocity as in Eq. (18). We may obtain the better results, predicting both the abnormal behavior near the critical point and the viscosity at the critical point if we know the exact value of $\gamma$.

## Conclusion

In spite of its practical and theoritical importance, few theories have been developed for the prediction of the viscosity at the critical point. The present study has led to the following conclusions.

(1) The viscosity theory previously proposed by the present authors seems to be the only one that can successfully predict the fluid viscosity at the critical point.

(2) This theory can be simplified in a simple form with no adjustable parameters, allowing easy calulation of the viscosity at the critical point, similar to the empirical formula by Bird.

(3) The agreements between the theoretical predictions and the experimental results are satisfactory.

## References

1. Hanley, H.; Mccarty, R. D. *Physica* **1972**, *60*, 356.
2. Reid, R. C.; Prausnitz, J. M.; Sherwood, T. K. *The Properties of gases & Liquids*; McGraw Hill: 1977.
3. Touloukian, Y. S.; Saxena, S. C.; Hestermaus, P. *Thermophysical Properties of Matter-TPRC Data Series*, Volume Viscosity; Purdue Reserch Foundation: 1975.
4. Stephan, K.; Lucas, K. D. *Viscosity of Dense Fluids*; Plenum Press: 1979.
5. Viswanath, D. S.; Natarajan, G. *Data Book on the Viscosity of Liquids*; Hemisphere Publishing: 1989.
6. Peri, R.; Ferrell, R. A. *Phys. Rev.* **1972**, *A6*, 2358.
7. Bird, R. B. *Transport Phenomena*; John Wiley & Sons, Inc.: 1960; p 17.
8. Kim, W.; Pak, H.; Chair, T. S. *Bull. Korean Chem. Soc.* **1989**, *10*, 372.
9. Kim, W.; Chair, T. S. *Bull. Korean Chem. Soc.* **2001**, *22*, 43.
10. Kim, W.; Chair, T. S.; Pak, H. *Bull. Korean Chem. Soc.* **1988**, *9*, 213.
11. Choi, D. S.; Kim, M. J.; Pak, H. *J. Korean Chem. Soc.* **1978**, *22*, 1.
12. Kim, S. H.; Kim, W.; Chair, T. S. *J. Korean Chem. Soc.* **1991**, *35*, 487.
13. Moor, W. J. *Physical Chemistry*; Prentice-Hall: Inc.: Englewood Cliffs, New Jergy, 1972; p 157.
14. Korsten, H. *Ind. Eng. Chem. Res.* **2000**, *39*, 813.
15. Hougen, O. A.; Watson, K. M. *Chemical Process Principles*, Part III; Wiley: New York, 1947; p 873.
16. Bird, R. B. *Transport Phenomena*; John Wiley & Sons, Inc.: 1960; p 744.