

DENSE FLUID VISCOSITY. A GENERALIZATION FROM MOLECULAR THEORY

Charles J. Vadovic and Kenneth E. Starling

School of Chemical Engineering and Materials Science, University of Oklahoma, Norman, Oklahoma

By making suitable approximations to the statistical mechanical expression for viscosity developed by Born and Green (1) a general form for viscosity is developed. When simultaneously applied to light hydrocarbons, methane through n-butane, the resulting equations reproduce the data over a wide range of conditions.

Modern theories of fluids (1-4) hold that the coefficient of viscosity should be expressed as the sum of two terms, i.e.,

$$\mu = \mu_K + \mu_V \quad \text{Eq. 1}$$

The terms μ_K and μ_V are usually referred to as the kinetic and intermolecular force contributions to viscosity, respectively. At low density, one is primarily concerned with the transfer of momentum due to the free motion of molecules between collisions. At high density momentum transfers due to intermolecular forces predominate. Both contributions are dependent on density and temperature. However, in the dilute gas limit, where the thermal motion of the molecules is the principal contribution, μ_K is a function of temperature only and the intermolecular force contribution is negligible. These conditions can be written as

$$\lim_{\rho \rightarrow 0} [\mu_K(T, \rho)] = \mu_O(T) \quad \text{Eq. 2}$$

and

$$\lim_{\rho \rightarrow 0} [\mu_V(T, \rho)] = 0 \quad \text{Eq. 3}$$

For computational purposes $\mu_K(T, \rho)$ will be assumed equal to $\mu_O(T)$, i.e., it does not vary to any great extent from the dilute gas value.

Born and Green (1) derived the viscosity coefficient in terms of integrals which can be written as

$$\mu = \frac{1}{30} \int \nu(r) \rho'(r) r^3 dr - \frac{1}{15} m \int \rho_2(v) v^4 dv \quad \text{Eq. 4}$$

The second term corresponds to the kinetic contribution and has already been assumed to equal $\mu_O(T)$. Thus, it is the first term in equation 4 with which we will be concerned.

In evaluating the integral, the first assumption made is that the nonequilibrium distribution function $\nu(r)$ is proportional to the radial distribution function at equilibrium, i.e.,

$$\nu(r) = \alpha_1 N_2^O(r) \quad \text{Eq. 5}$$

From purely dimensional considerations the proportionality factor α_1 , is given by

$$\alpha_1 = K_1 \left(\frac{1}{r}\right) \left(\frac{m}{kT}\right)^{1/2} \quad \text{Eq. 6}$$

Thus,
$$\mu_V = K_1 \frac{2\pi}{15} \left(\frac{m}{kT}\right)^{1/2} \int N_2^O(r) \rho'(r) r^4 dr \quad \text{Eq. 7}$$

From an analysis of the plot, given in Figure 1, of the radial distribution function and the derivative of the potential function, it is found that this product can be approxi-

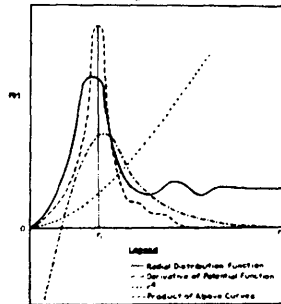


FIGURE 1. Functions of intermolecular distance.

mated by a gaussian type curve with a maximum at the average intermolecular distance r_1 . This type of function has been integrated and is

$$\int n_2^0(r) \phi'(r) r^4 dr = n_2^0(r_1) \phi'(r_1) r_1^4 (w/\beta)^{1/2} \quad \text{Eq. 8}$$

where

$$\beta = \sigma^2 \{ \ln n_2^0(r) + \ln \phi'(r) + 4 \ln(r) \} / dr^2 \Big|_{r=r_1} \quad \text{Eq. 9}$$

Before proceeding further, it is necessary to choose models for the radial distribution function and the potential function. The Lennard-Jones potential model,

$$\phi(r) = 4\epsilon \left[(\sigma/r)^{12} - (\sigma/r)^6 \right] \quad \text{Eq. 10}$$

is utilized. It is assumed that only the attractive portion of this model contributes to the viscosity or $\phi'(r) = 6\gamma/r^7$ Eq. 11

TABLE 1. Individual light hydrocarbon parameters.

Material	$\epsilon/k, ^\circ K$	$\sigma, \text{\AA}$	w	K_1	Std. Dev.
Ethane	262.0	4.238	0.608	0.533	2.5%
Propane	346.0	4.668	0.613	0.574	3.5%
n-butane	410.0	4.997	0.608	0.585	3.6%

The radial distribution function is approximated by

$$n_2^0(r) = n^2 \exp[-\phi(r)/kT] \quad \text{Eq. 12}$$

Thus β can be reduced to

$$\beta = \left(42\gamma/r_1^8 kT \right) + \left(3\gamma/r_1^2 \right) \quad \text{Eq. 13}$$

The second term in Equation 13 can be neglected at moderate temperatures, so that equation 8 becomes

$$\mu_v = K_1 \left(2w/105 \right) (42\gamma m^2)^{1/2} n^2 r_1 \exp(\gamma/r_1^6 kT) \quad \text{Eq. 14}$$

Now one can relate the average intermolecular distance to the density through the concept of a packing factor (3). Thus, r_1 is given by

$$r_1 = w^{-1/3} (N_0/M)^{-1/3} \quad \text{Eq. 15}$$

The intermolecular force contribution to viscosity can then be written as

$$\mu_v = K_1 (2w/105) (42\gamma m^2)^{1/2} (w^{5/3}/m^{5/3} N_0^{1/3}) \quad \text{Eq. 16}$$

$$\exp(w^2 \rho^2 / m^2 kT)$$

Therefore, the viscosity at any temperature and density is simply the sum of $\mu_o(T)$ and the above result.

In order to test the usefulness of the developed expression for viscosity, the final equation was applied to individual light hydrocarbons. A nonlinear least squares technique was used to evaluate the parameters, K_1 and w , for ethane through n-butane. It was found that there are, indeed, values of the parameters which are capable of reproducing the data with fairly close agreement. These results are summarized in Table 1, along with the Lennard-Jones

parameter values (3) used in the calculation.

The data used to obtain these results cover the ranges 77° to 340°F and 14.7 to 8000 psia. From the standard deviations listed there can be no doubt that the temperature and density dependence of equation 15 is reasonably good over the indicated ranges. The results in Table 1 also demonstrate the possibility of utilizing universal values for K_1 and w . With this in mind, further calculations were made with methane, ethane, propane, and n-butane data (5) used simultaneously to determine the parameters K_1 and w . The Lennard-Jones parameter values (6) used in these calculations for methane are $\epsilon/k = 144.0^\circ K$ and $\sigma = 3.796^\circ A$. These calculations showed that it is possible to describe the viscosity of all four light hydrocarbons using a com-

mon set of values for K_1 and w . These results are listed in Table 2.

TABLE 2. Generalized parameters for light hydrocarbons.

Materials	C ₁ to n-C ₄
Temperature Range	100° to 340°F
Pressure Range	14.7 to 5000 psia
w	0.573
K_1	0.621
Standard Deviation	3.28%

The most encouraging aspect of this study is the fact that the constants introduced into the derivation evidently are universal for a given class of compounds. These constants were introduced in the assumptions made to transform the microscopic expression for viscosity, given in terms of intermolecular separation, into a macroscopic expression in terms of density. The adequacy of such assumptions can only be established by a comparison with data; however, ensuing calculations can and do lend credence to the proposed approximations. This method of attack can also be applied to mixtures and other transport properties. Preliminary calculations for thermal conductivity have yielded encouraging results. The major conclusion to be made is that the molecular theory of fluids provides an excellent basis for the prediction of transport properties.

NOMENCLATURE

K_1	—Parameter in equation for viscosity
M	—Molecular weight
N	—Avogadro number
P	—Absolute Pressure
R	—Universal gas constant
T	—Absolute temperature
k	—Boltzmann's constant
N_2^0	—Radial distribution function

r	—Intermolecular distance
v	—Molecular velocity
w	—Parameter in equation for viscosity
β	—Relative standard deviation of data
γ	—Constant in attraction part of potential function
ϵ	—Parameter in Lennard-Jones potential function
μ	—Coefficient of viscosity
μ_0	—Dilute gas viscosity
μ_K	—Contribution to viscosity due to the motion of molecules between collisions
μ_V	—Contribution to viscosity due to the action of intermolecular forces
$\nu(R)$	—Function of intermolecular distance
π	—The constant 3.1416
ρ	—Mass density
σ	—Parameter in Lennard-Jones potential function

REFERENCES

1. M. BORN and H. S. GREEN, *A General Kinetic Theory of Liquids*, Cambridge University Press, London, 1949.
2. H. S. GREEN, *Molecular Theory of Fluids, Interscience*, New York, 1952.
3. K. E. STARLING, *Viscosity of Dense Fluids*, Ph.D. Dissertation, Illinois Institute of Technology, Chicago, 1962.
4. K. W. STARLING and R. T. ELLINGTON, A. I. Ch. E. (Am. Inst. Chem. Engrs.) J. 10: 11-15 (1964).
5. A. L. LEE, *Viscosity of Light Hydrocarbons*, American Petroleum Institute, New York, 1965.
6. J. O. HIRSCHFELDER, C. F. CURTIS, and R. B. BIRD, *Molecular Theory of Gases and Liquids*, John Wiley & Sons, Inc., New York, 1967.