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A CALCULATION FOR THE VISCOSITY OF FLUIDS BY USING VAN DER WAALS EQUATION OF STATE

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Abstract—A new equation for the viscosity of fluid is presented by considering that the viscosity is equal to the product of the shear pressure and the shear relaxation time. The shear pressure and the shear relaxation time are calculated thermodynamically by applying the van der Waals model for fluids. The calculated viscosities for various simple substances are in good agreements with those of the observed values through liquid-critical point-gas region.

INTRODUCTION

It is well known that the viscosity of fluid is an important property to illustrate the transport phenomena of physical, chemical and biological system. Much efforts have been pursued by many physicists, chemists, chemical engineers, and biotechnologists to solve this interdisciplinary problem. Gas viscosities at low pressure can be estimated by techniques based on the kinetic theory [1], but there is no comparable theoretical basis for the estimation of viscosity of liquids. Certainly the viscosities of liquids are considerably different from those of gases i.e., they are much larger numberically, and they decrease sharply with an increase in temperature. The phenomenon of low-pressure gas viscosity is primarily due to the transfer of momentum by individual collisions between molecules moving randomly between layers with different velocities. A similar momentum transfer may also exist in liquids, although it is usually overshadowed by the interacting force fields between the close-packed liquid molecules.

The study of viscosity began in 1687 with Sir Isaac Netwon. However, in liquids, until 1930, only a handful of semiempirical formulas existed with which to describe the temperature dependence of the viscosity, and none at all capable of calculating liquid viscosity values from elementary molecular data. Since 1930, inquiries into the nature of the liquid state have met with considerable success, and analytic representations of the viscosity of liquids have flourished in a corresponding fashion.

In the 1930's Andrade [2] advanced a model from which he was able to deduce a formula giving the viscosity of a liquid at its freezing point, and from which the temperature dependence of the viscosity could be predicted. Eyring [3] based his 1936 analysis [4] of the viscous mechanism on chemical kinetics, and found agreement with experiment in certain cases.

On the other hand, the beginnings of the modern statistical theory of transport processes in liquids were set forth by Enskog in 1936 and by Kirkwood [5] in 1946, and refined by many subsequent investigators. Although the Kirkwood approach appeared to be very successful for many years, ultimating in the Rice-Allnatt theory [6] of transport, recent work has shown that there are serious flaws [7] in the theory. No theory, as yet, reduces to a simple form which can be applicable to both phases of gas and liquid.

In this paper, a fundamental equation of viscosity of fluids is proposed, which can be applicable to both phases of liquid and gas including the critical point for the Newtonian flow.

THEORY

Let a shear stress σ be applied with a shear rate $\dot{s}$ to a fluid which constains N molecules in a volume V at the temperature T. If the resulting flow is a Newtonian, the shear viscosity defined by

$$\eta = \frac{\sigma}{\dot{s}} \tag{1}$$

is independent of the shear rate. The shear stress is the force applied per unit area, while the inverse of the shear rate $\frac{dt}{ds}(=\tau)$ is the time required to produce unit strain. Therefore, we call the former the shear pressure and the latter the shear relaxation time. Then, the viscosity can also be expressed as

$$\eta=\tau\sigma. \tag{2}$$

The viscosity is a resistance against the flow and it is a property characteristic to the fluid itself. It may come both from the kinetic molecular motions and the intermolecular interaction. Let the former part be denoted by η_k and the latter by η_i to have

$$\eta=\eta_k+\eta_i. \tag{3}$$

It the former part is proportional to the kinetic pressure σ_k, the latter is also proportional to the internal pressure σ_i as follows;

$$\eta_k=\xi_k\tau\sigma_k \tag{4}$$

$$\eta_i=\xi_i\tau\sigma_i \tag{5}$$

where ξ_k and ξ_i are proportionality factor, and they should be the same.

The kinetic and the internal pressure of the fluid molecules are related to the thermodynamic properties of the system as follows:

$$\sigma_k=T\left(\frac{\partial P}{\partial T}\right)_v=T\frac{\alpha_P}{\beta_T} \tag{6}$$

$$\sigma_i=\left(\frac{\partial E}{\partial V}\right)_T=T\frac{\alpha_P}{\beta_T}-P. \tag{7}$$

In conjunction with the shear relaxation time, we assume that the time is inversely proportional to the velocity of phonon propagating through the fluid.

$$\tau=\xi v_{ph}^{-1}\lambda_{ph} \tag{8}$$

where v_{ph} is the phonon velocity for which we take the sound velocity $(\gamma/\rho\beta_T)^{1/2}$. The latter may be expressed as

$$\lambda_{ph}=1/(\pi d^2\eta_{ph}) \tag{9}$$

where d and η_{ph} are the inter-phonon collision diameter and the phonon number density, respectively. For the phonon number density η_{ph}, we assume that it is proportional to the number density N/V as

$$\eta_{ph}=f(N/V) \tag{10}$$

where the proportionality factor f is taken equal to the vacancy fraction in the fluid $(V-V_s)/V$, V_s being the fluid volume at the closeset packed state. For the Newtonian flow, the value $\xi_k\times\xi$ should be unity to have the viscosity which is independent of the external force.

By introducing eqs 2 through 9 into eq. (1), we have

$$\eta=(2T\alpha_p/\beta_T-p)\,(\rho\beta_T/\gamma)^{1/2}\,(\pi d^2\eta_{ph})^{-1} \tag{11}$$

All the quantities included in the right hand side of eq. (11) are the intrinsic properties for the fluid in equilibrium state so that we can find them by applying the equilibrium thermodynamics.

VAN DER WAALS MODEL

For the calculation of the fluid viscosity by using eq. (11), we have to know the thermodynamic properties such as p, α_P, β_T, and γ for the canonical system. Unfortunately, the theory which can be applicable to both of liquid and gas phases is not found yet. Therefore, as the first approximation, we test out viscosity equation by using the simple van der Waals model in this paper.

According to van der Waals model, the kinetic and the internal pressures are given as follows;

$$T\left(\frac{\partial P}{\partial T}\right)_v=\frac{RT}{V-b} \tag{12}$$

$$\left(\frac{\partial E}{\partial V}\right)_T=\frac{a}{V^2}. \tag{13}$$

The parameter b is approximately related to the collision diameter as

$$b=(1/\sqrt{2})\,d^3N. \tag{14}$$

The collision diameter d is modified as follows,

$$d=d^*(1+0.8T_c/T) \tag{15}$$

which is the same as the Sutherland correction. Where d* is a parameter which can be determinded by putting the value of d at the critical temperature T_c into eq. (15).

The parametric values of d* and b for various fluids are listed in Table 1.

By using eq. (11) and the van der Waals model, we can calculate the viscosities of gas and liquid for various substances. In the critical region, we can obtain the following reduced viscosity equation

$$\eta_r=\frac{V_r^{2.5}}{\gamma^{1/2}(\frac{8}{3}V_r^3T_r-6(V_r-1/3)\}^{1/2}}\left(\frac{1.5T_r}{V_r-1/3}+\frac{1.7}{V_r^2}\right)$$
$$=\frac{V_r^{2.5}\{0.57(P_r+3/V_r^2)+1.7/V_r^2\}}{\gamma^{1/2}(V_r-1/3)\{V_r^3(P_r+3/V_r^2)/(V_r-1/3)-6\}^{1/2}}. \tag{16}$$

RESULT AND DISCUSSION

In Fig. 1-5, the calculated liquid and gas viscosities

Table 1. Parametric values used in calculation

	Ar	N_2	CH_4	CCl_4	C_6H_6
d/A°	3.418[a]	3.749[a]	3.882[a]	5.881[a]	5.27[a]
b/cm^3	24.97	29.83	33.00	92.00	86.33
b^c/cm^3	26.54	30.84	33.83	92.18	86.33

a: Parameters taken from Ref. 20
c: Adjusted value of b

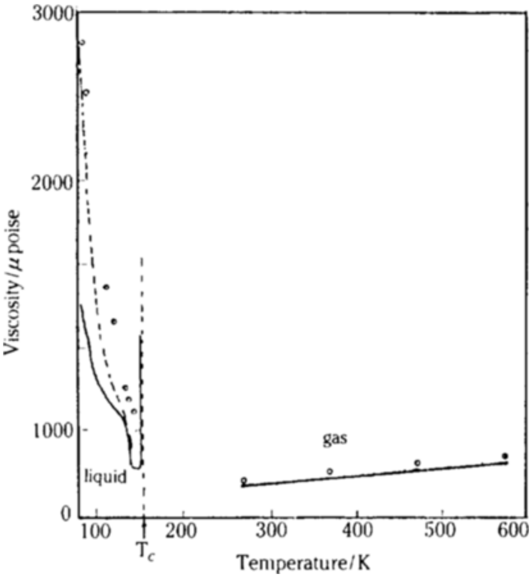

Fig. 1. Viscosity of Argon for gas and liquid.
Solid line; Calculated, Open circles; Observed [Ref. 21 (for liquid), Ref. 8 (for gas)].
Chain curve: the parameter b is fitted (Table 1).
The viscosity is diverged at the critical point.

of argon, nitrogen, methane, benzene, and carbon tetrachloride are compared with those of the observed values [8,9]. As the figure shown, the agreements between the calculated and the observed ones are fine though some deviations occur. This deviation may be minimized if we adjust the van der Waals constant b to fit the calculated liquid viscosities to the observed ones. Since the van der Waals equation of state is not good enough to illustrate liquid state, we may choose another equation of state for liquid. With this eq. (11), good calculated results of the viscosity could have been acquired by using real values of α_p and β_T [19].

The calculated reduced viscosities in the critical region by using eq. (16) are plotted against the reduced temperature for the various reduced pressure in Fig. 6.

Notwithstanding the use of the van der Waals equation of states, the calculated viscosities are in good

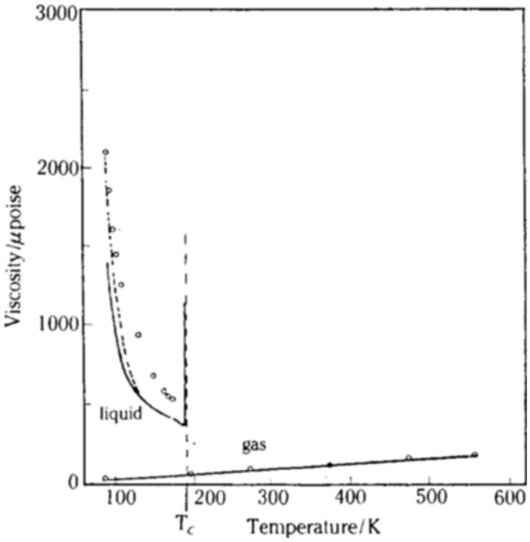

Fig. 2. Viscosity of nitrogen for gas and liquid.
The notation is the same to the Figure 1.

agreements with those of the observed ones through the liquid-critical point-gas region. We expect that we can obtain the better results by finding out the better state equation for fluid.

We can find various abnormality of fluid viscosity [10,11] such as abrupt increase near the critical point (Fig. 1-3), an abnormal tendency of viscosity-pressure curve of liquid water near 0-20°C [12,13], and the su-

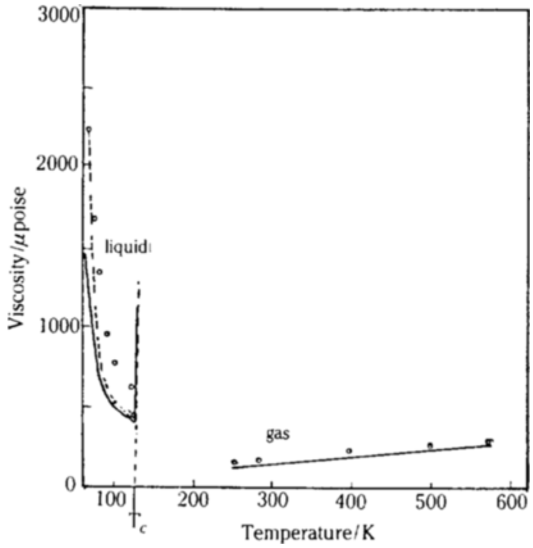

Fig. 3. Viscosity of methane for gas and liquid.
The notation is the same to the Figure 1.

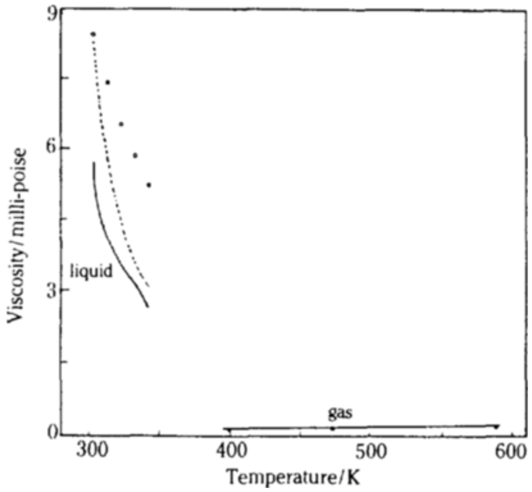

Fig. 4. Viscosity of carbon tetrachloride for gas and liquid.

The notation is the same to the Figure 1.

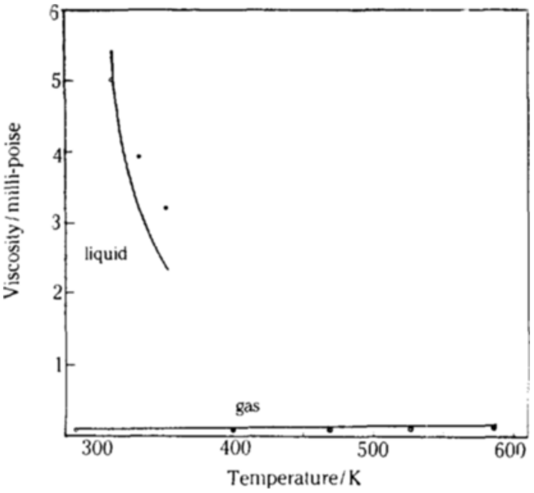

Fig. 5. Viscosity of benzene for gas and liquid.

Solid line; Calculated, Open circles: Observed [Ref. 21 (for liquid), Ref. 8 (for gas)].

perfluidity of liquid ^{4}He [14]. All of the above abnormalities of viscosity can be explained by eq. (11), though the calculated results are not shown in this paper.

We also expect that the abnormal character of thermal conductivity near critical region [15], the viscosity of fluid mixture and the other transport properties can be explained by using our viscosity equation.

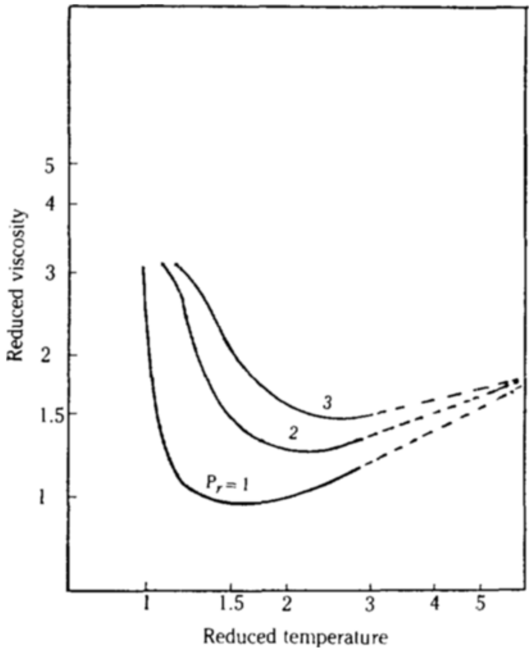

Fig. 6. Reduced viscosity as a function of reduced temperature for several values of the reduced pressure.

C_p values are taken from Ref. 16.

$\eta_c = 61.6 \cdot (MT_C)^{1/2} \cdot (V_c)^{-2/3}$ (Ref. 18)

NOMENCLATURE

a : van der Waals constant
b : van der Waals constant
d : inter-phonon collision diameter
E : internal energy
N : Avogadro number
η_{ph} : phonon number density
P_r : reduced pressure
R. : gas constant
$\dot{s}$: shear rate
T_r : Reduced temperature
V_{ph} : phonon velocity
V_s : fluid volume at the closest packed state
V_r : reduced volume

Greek Letters

α_P : isobaric expansion coefficient
β_T : isothermal compressibility
γ : heat capacity ratio (C_p / C_v)
σ : shear stress
σ_k : kinetic pressure
σ_i : internal pressure

ρ : mass density
λ_{ph} : mean free path of the phonon
ξ : proportionality factor
η_r : reduced viscosity

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