A Study on the Abnormal Behavior of the Viscosity near the Critical Point

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The new viscosity theory is applied to the abnormal behavior of the viscosity near the critical point. This theory suggests that the viscosity is equal to the product of the absolute pressure(kinetic pressure + internal pressure) and the collision time. We can find this abnormal behavior to be due to the large collision time near the critical point. The agreements between theoriticals and experimentals of the critical enhancement are satisfactory.

Introduction

Since Maxwell proposed a theory of viscosity of gas based on the idea of a mean free path at 1860, various expressions for the viscosity of fluids have been presented. Representative examples are the expressions based on the kinetic theory of Chapman-Enskong[1], the model theory of Frenkel[2], Eyring[3] and Andrade[4], the corresponding state theory of Helfand and Rice[5], the hard sphere theory of Longuet-Higgins and Pople[6] and so forth. At the present time the approximate theory of Enskog is the most usable for describing the viscosity of real gases. The viscosity of liquids, on the other hand, are best described by the Eyring theory of absolute reaction rates. None of these expressions, however, provide satisfactory results in dense gas regions including the critical point.

Many thermophysical properties exhibit an anomalous behavior in the vicinity of the critical point. For instance, the isothermal compressibility, the thermal expansion coefficient and the specific heat of fluids all diverge at the critical point. Anomalous effects are also encountered when one studies the behavior of the viscosity of fluids near the critical point. Nevertheless, the experimental evidence indicates that the shear viscosity diverges at the critical point[7]. The explanation for this phenomenon is not clear. Some decoupled theories[8,9] had been applied to the critical viscosity with little success. In this paper we apply our viscosity equation (10) to fluids near the gas-liquid critical point by adapting the van der Waals equation of state.

Theory

According to our previous theory[10] the viscosity of fluid, through which a phonon propagates with a velocity V_{ph} and a free path λ_{ph}, can be given as follows

$$\eta = (P_k + P_i)\,\lambda_{ph}/V_{ph} \tag{1}$$

where P_k and P_i are the kinetic and the internal pressures of the molecules. To find out these pressures we have to have the equation of 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 the van der Waals equation of state as follows;

$$P = \frac{RT}{V-b} - \frac{a}{V^n} \tag{2}$$

where a and b are the van der Waals constants and n is a parameter which is equal to 2 for the van der Waals gas. These parameters can be found by applying the critical boundary conditions as follows,

$$n = 2Z_c + (4Z_c^2 + 1)^{1/2} \tag{3}$$

$$a = \frac{n+1}{n-1} P_c V_c^n \tag{4}$$

$$b = \frac{n-1}{n+1} V_c \tag{5}$$

where Z_c, P_c and V_c are the compressibility factor, the critical pressure and the critical volume, respectively. By using equation(2), we have

$$P_k = \frac{RT}{V-b} \tag{6}$$

$$P_i = \frac{a}{V^n} \tag{7}$$

In conjunction with the phonon, we have

$$\lambda_{ph} = (\pi d^2 N_{ph})^{-1} \tag{8}$$

$$V_{ph} = (\gamma/\rho\beta_t)^{1/2} \tag{9}$$

where N_{ph} is the phonon number density, ρ is the fluid density and β_T is the isothermal compressibility. By using eqs (1) through (9) we can find the reduced viscosity equation as follows

$$\eta_r = \frac{0.27\,V_r^{1.5+\frac{n}{2}}}{\delta^{3/2}\gamma^{1/2}\left[\dfrac{4n}{n^2-1}V_r^{n+1}T_r - \dfrac{n}{\delta}(V_r - \dfrac{1}{\delta})^2\right]^{1/2}} \left(\frac{\dfrac{4n}{n^2-1}T_r}{V_r - \delta} + \frac{1}{V_r^n\delta}\right) \tag{10}$$

where η_r, V_r, T_r and δ are the reduced viscosity, reduced volume, reduced temperature, and $\dfrac{n-1}{n+1}$, respectively.
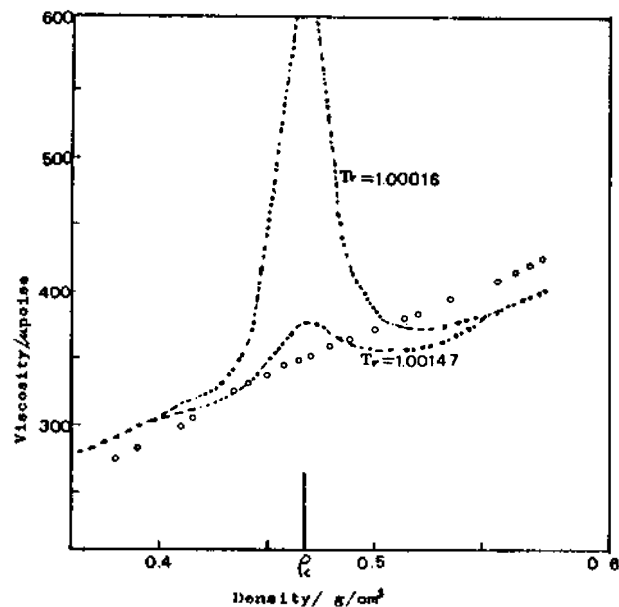
Result and Discussion

In the critical region we found that the heat capacity ratio γ for nitrogen, carbon dioxide and ethane is expressed as

$$\gamma^{-1} = 3.8 \times 10^{-4} + 0.39|\,T_r - 1| + 0.28|1 - \rho_r|^{2.1} \tag{11}$$

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Table 1. Parameters used in Calculation

	$a \times 10^{-5}$/atm·cm^3	b/cm^3	n
Nitrogen	3.03	24.05	1.74
Carbon dioxide	6.09	24.05	1.69
Ethane	9.85	61.96	1.72
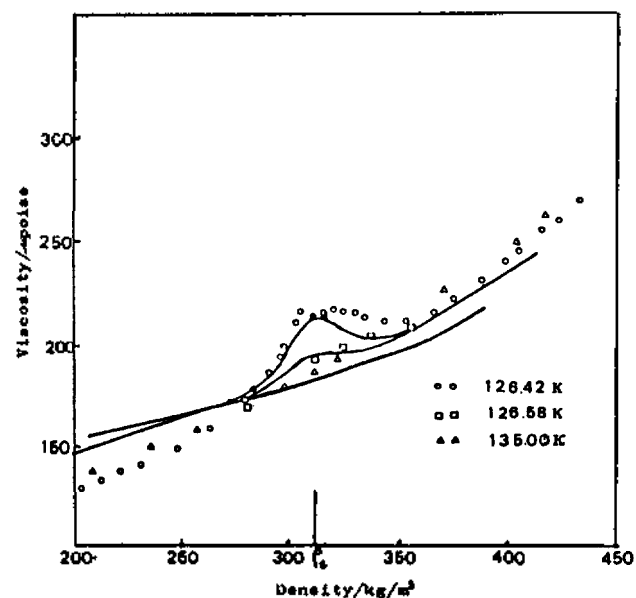
Figure 1. Viscosity of nitrogen as a function of density near the critical point (T$_c$ = 126.20K). Calculated; solid line, Observed; circles (T = 126.42K), triangles (T = 135.00K), and quadrangles (T = 126.58K) (Ref. 7).
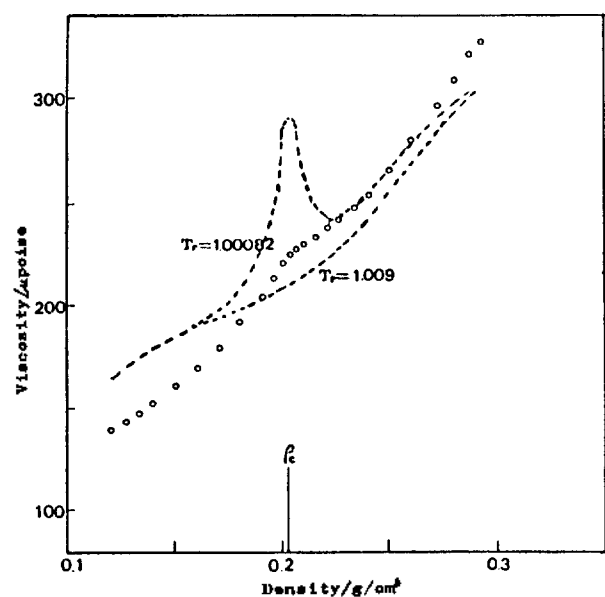
Figure 2. Viscosity of ethane as a function of density near the critical point (T$_c$ = 305.40K). Calculated; broken line, Observed; circles (Ref. 11).

where ρ_r is the reduced density. The parametric values *a*, *b* and *n* used for nitrogen, carbon dioxide and ethane are listed

Figure 3. Viscosity of carbon dioxide as a function of density near the critical points (T$_c$ = 304.20K). Calculated; broken line, Observed; circles (Ref. 11).
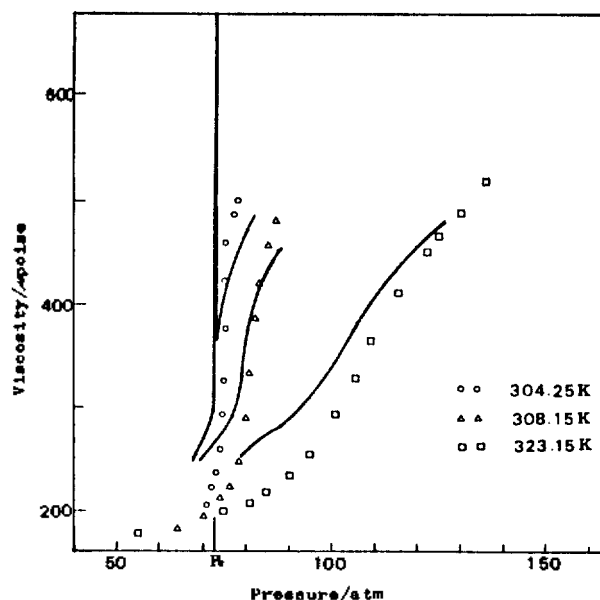
Figure 4. Viscosity of carbon dioxide as a function of pressure near the critical point. Calculated; solid line, Observed; circles (T = 304.25K), triangles (T = 308.15K), and quadrangles (T = 323.15K) (Ref. 11).

in Table 1. The calculated values of viscosity near the critical point are in good agreements with those of the experimental data as shown in Figure 1 through 3. We can find much more anomalous enhancement in viscosity according as the temperature is approached to the critical temperature as shown in Figure 1. We can also predict that the calculated viscosity diverges at the critical point as the experimental evidence proposed. In Figure 2 and 3, the experimental values of viscosity[11] of ethane and carbon dioxide indicate a slow enhancement near the critical point, but is not sensitive comparing with the viscosity of nitrogen. It is because that the
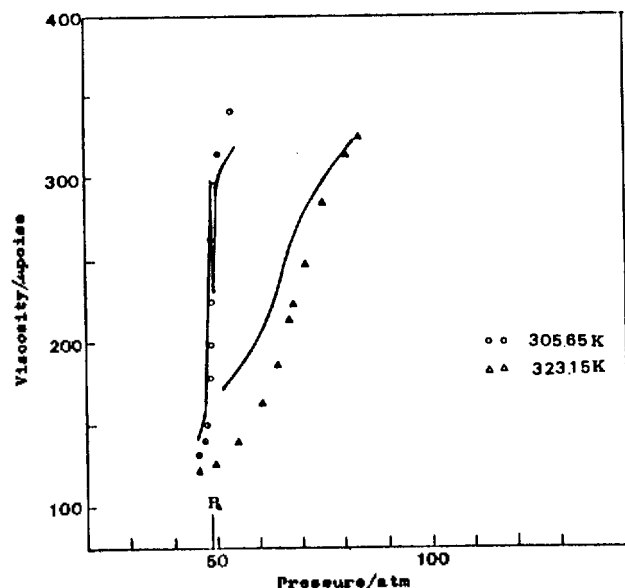
Figure 5. Viscosity of ethane as a function of pressure near the critical point. Calculated; solid line, Observed; circles (T = 305.65 K), triangles (T = 323.15K) (Ref. 11).

pressure) of fluids and the collision time. Accordingly the magnitude of viscosity depends on the value of the kinetic pressure, internal pressure and the collision time. The viscosity of fluids depends only on the collision time when the fluid has the same kinetic and internal pressure. Near the critical point the phonon velocity is so slow that the viscosity can be seen to present the abnormal behavior because of the large collision time. At the critical point the phonon velocity is zero, so we can see the viscosity of fluids diverge due to the infinitely large collision time. This new methodology of the viscosity interpretation is not the same as the previous theories. We hope this equation is useful to explain the true nature of viscosity of fluids including the critical region.

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experimental methods, such as the capillary flow method for measuring the viscosity, become inaccurate in the critical region due to the large compressibility. Figure 4 shows a plot of the viscosity of carbon dioxide against the pressure at 304.25K 308.15K, and 323.15K. Both the calculated and observed values indicate the rapid increase near the critical point. Figure 5 shows a plot of the viscosity of ethane against the pressure near the critical point. The agreements between theory and experiment are good as those for carbon dioxide.

For the phenomenon of anomalous enhancement in viscosity near the critical point, we can explain as follows. The viscosity of fluids can be considered to be equal to the product of the absolute pressure(kinetic pressure + internal

The Double Photodissociation of a Geminal, Dichloride

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Photolysis of dichlorodiphenylmethane in glassy 2-Me THF at 77K results in the formation of diphenylcarbene and the diphenylchloromethyl radical, which were detected by their fluorescence emission and excitation spectra. The relative yield of the carbene to radical is shown to vary dramatically as a function of irradiation time. The photolability of the radical is also demonstrated. These results were interpreted in terms of a two step mechanism, where the diphenylchloromethyl radical is an intermediate in the formation of diphenylcarbene.

Introduction

The photodissociation of benzylic halides to produce arylmethyl radicals is a well known process. By photolysis of ap-

propriate arylmethyl halides, various arylmethyl radicals including benzyl[1], naphthylmethyl[2] and diphenylmethyl[3] have been produced and spectroscopically characterized. The photodissociation is believed to be initiated by promotion to