A Paradigm for the Viscosity of Fluids

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A new paradigm for the viscosity of fluid is presented by considering the fact that the viscosity is equal to the shear stress divided by the shear rate. The shear stress is obtained from the sum of kinetic and internal pressures of fluid, and the shear rate is found from the phonon velocity divided by the mean free path of the phonon. The calculated viscosities for various simple substances are in excellent agreements with those of the observed data through the wide temperature range covered both of liquid and gas phase.

Introduction

In the 1860th, Maxwell proposed a theory of viscosity of gas based on the idea of a mean free path introduced earlier by Clausius. This theory shows that the gas viscosity is independent of the density and proportional to the square root of the absolute temperature. In the later theory, Maxwell was able to shown that the gas viscosity is proportional to the temperature of considering the inverse fifth power repulsion force[1]. In 1921, Enskog and Chapman[2] obtained the similar viscosity equation by solving the Boltzmann equation for the dilute gas.

Following the acceptance of Maxwell's theory of gas viscosity and its later refinements by Enskog and Chapman, it has been customary to begin theoretical discussion of liquid viscosity by pointing out that the mechanism of momentum transport in a liquid must be different from that in a gas. Since the density of a liquid is usually so high that the momentum transfer in liquid may occur by the action of the intermolecular forces of the neighbors, while in a gas the molecules transport their momentum by their own motion from one layer to another. Some formal approaches to the liquid viscosity were done by considering the intermolecular forces in liquid[3]. However, no general theory of viscosity which can be applicable to both phases of gas and liquid has been developed until now.

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 α be applied with a shear rate s to a fluid which contains N molecules in a volume V at the temperature T. If the resulting flow is a Newtonian, the shear viscosity defined by

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

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

$$\eta=\eta_K+\eta_1 \tag{2}$$

where η_K and η_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 η_K and η_I may be proportional to the corresponding pressures as

$$\eta_K=\xi_K p_K/s$$

$$\eta_1=\xi_I p_I/s \tag{4}$$

where p_k and p_I are the kinetic and the internal pressures of the fluid respectively and ξ is the proportionality factor which may be related to the external forces.

The kinetic and the internal pressures are given by

$$p_K=T(\partial P/\partial T)_V=T\alpha_P/\beta_T \tag{5}$$

$$P_I=(\partial E/\partial V)_T=T\alpha_P/\beta_T-P$$

where p, E, α_P, and β_T are the equilibrium pressure, the internal energy, the isobaric expansion coefficient, and the isothermal compressibility of the fluid respectively.

In conjunction with the shear rate, we assume that the rate is proportional to the velocity of phonon propagating through the fluid as

$$s=\xi V_{ph}/\lambda_{ph} \tag{7}$$

where v_{ph} is the phonon velocity for which we take the sound velocity ($\gamma/\rho\beta_T$) , γ being the heat capacity ratio C_p/C_v and , the mass density of the fluid, and where λ_{ph} is the mean free path of the phonon. The latter may be expressed as

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

where d and n_{ph} are the inter-phonon collision diameter and the phonon number density respectively. For the Newtonian flow, the proportionality factor ξ in eqs 3, 4 and 7 should be the same to have the viscosity which is independent of the external force.

By introducing eqs 2 through 8 into eq. 1, we have

$$\eta=(2T\alpha_P/\beta_T-P)\ (\rho\beta_T/\gamma)^{1/2}\ (\pi d^2 n_{ph})^{-1} \tag{9}$$

All the quantities included in the right hand side of eq. 9 are the intrinsic properties for the fluid in equilibrium state so that we can find them by applying the equilibrium thermodynamics.

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Table 1. Parametric Values used in Calculation

	Ar	N_2	CH_4	CCl_4	C_6H_6	CS_2	$(CH_3)_2CO$
d°/Å	3.418[a]	3.749[a]	3.882[a]	5.881[a]	5.349[b]	4.483[b]	5.30[c]
V_s/cm^3	26.42	30.76	34.00	91.92	84.81	54.56	67.59

[a] Parameters taken from Ref. 9 [b] Parameters taken from Ref. 5 p. 678 [c] Parameter obtained by fitting the calculated viscosity to the observed one.

Calculation and Result

To calculate the viscosity of fluids by using eq. 9, we take an approximation for d as follows;

$$d=d^{\circ}(1+1.8T_b/T)^{1/2} \tag{10}$$

which is the same as the Sutherland's[4] correction equation for the intermolecular collision diameter except the proportionality constant 1.8, T_b being the normal boiling temperature of liquids. The parametric value d° can be taken equal to that of Sutherland's one.

For the phonon number density n_{ph}, we assume that it is proportional to the number density N/V as

$$n_{ph}=f(N/V) \tag{11}$$

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 closest packed state.

The parametric values of d^o and V_s for various fluids are listed in Table 1. The experimental data of α_p, β_T, and C_p for the fluids are listed in Tables 2 through 8. As shown in those tables, the calculated viscosities of argon, nitrogen, methane, carbon tetrachloride, benzene, carbon disulfide, and acetone are in good agreements with those of the experimental data through the wide temperature range of liquid and gas phases. We can also find the excellent agreements in Figure 1.

Discussion

The viscosity equation (eq. 9) can be applied successfully to liquid and gas phases. To calculate the viscosities by using the equation, we have to have the data of α_P, β_T, and γ. These values can be calculated if we have a partition function for the fluid. Since we cannot find the simple partition function for liquids yet, we used the observed data for the calculation of liquid viscosity. For dilute gas, we obtained the values of α_P and β_T by using the equation of state of ideal gas, as 1/T and 1/P respectively.

It may remain some arguments in using the approximations of eq. 10 and 11, since these equations are the kinds of semiempirical. One may find the better approximations for d and n_{ph}. The values of d^o used in this paper are the ones for

Table 2. Comparison of calculated and observed Viscosities of liquid and Gas for Agron

Liquid state									Gas state				
T K	P^a bar	V^a cm^{3}mol^{-1}	$10^3\alpha_p^a$ K^{-1}	$10^4\beta_T^a$ bar^{-1}	C_p^a JK^{-1}mol^{-1}	$\eta_{calc.}$ μP	$\eta_{obs.}^b$ μP	Δ%	T K	C_p^c cal mol^{-1}	$\eta_{calc.}$ μP	$\eta_{obs.}^d$ μP	Δ%
85	0.97	28.39	4.42	2.088	41.9	2735	2750	–0.5	273	4.968	212	209.6	1.1
87.28	1.01	28.69	4.47	2.189	42.9	2492	2520	-1.1	373	4.968	274	269.5	1.7
90	1.34	29.04	4.57	2.330	43.6	2280	2320	-1.7	473	4.968	330	332.3	2.4
100	3.25	30.47	5.21	3.154	46.3	1780	1730	2.9	575	4.969	380	368.5	3.1
110	6.67	32.21	6.22	4.600	49.1	1483	1380	7.5	674	4.969	425	411.5	3.3
120	12.13	34.43	7.91	7.340	53.0	1274	1160	9.8	766	4.970	464	448.4	3.5
									857	4.970	500	481.5	3.8
									987	4.970	548	525.7	4.2
									1100	4.976	587	563.2	4.2

[a] Values taken from Ref. 10 [b] Values are the interpolated ones of Ref. 16 [c] Values taken from Ref. 5 p. 629 [d] Values taken from Ref. 12.

Table 3. Comparison of calculated and observed Viscosities of liquid and Gas for Nitrogen

Liquid state									Gas state				
T K	P^a bar	V^a cm^{3}mol^{-1}	$10^3\alpha_p^a$ K^{-1}	$10^4\beta_T^a$ bar^{-1}	C_p^a JK^{-1}mol^{-1}	$\eta_{calc.}$ μP	$\eta_{obs.}^b$ μP	Δ%	T K	C_p^c cal mol^{-1}	$\eta_{calc.}$ μP	$\eta_{obs.}^d$ μP	Δ%
65	0.174	32.54	4.48	1.97	56.5	2154	2180	-1.2	251.6	7.07	160	156.3	2.1
70	0.366	33.32	4.96	2.40	56.9	1709	1760	-2.9	284.1	7.10	174	170.7	1.9
77.35	1.013	34.64	5.70	3.22	57.7	1335	1360	-1.8	400.3	7.35	230	219.1	4.9
80	1.370	35.18	5.99	3.60	58.0	1239	1230	0.7	499.8	7.77	274	255.9	7.1
90	3.607	37.55	7.31	5.59	60.1	1002	960	4.4	572.1	8.20	304	279.7	8.7
100	7.789	40.68	9.53	9.74	64.7	853	750	13.7	763.2	9.93	379	337.4	12.3
110	14.67	45.20	14.1	20.2	75.7	751	610	23.2	1098.1	15.29	498	419.2	18.8
115	19.39	48.50	19.5	35.0	88.0	710	570	24.6					
126.2[e]	33.50	89.50	∞	∞	∞	∞	∞						

[a] Values taken from Ref. 10 [b] Values are the interpolated ones of Ref. 16 [c] Values taken from Ref. 5 p 629 [d] Values taken from Ref. 12 [e], critical point.

Table 4. Comparison of calculated and observed Viscosities of liquid and Gas for Methane

Liquid state									Gas state				
T K	P^a bar	V^a cm^{3}mol^{-1}	$10^3\alpha_p^a$ K^{-1}	$10^4\beta_T^a$ bar^{-1}	C_p^a JK^{-1}mol^{-1}	$\eta_{calc.}$ μP	$\eta_{obs.}^b$ μP	Δ%	T K	C_p^c cal mol^{-1}	$\eta_{calc.}$ μP	η_{obs}^d μP	Δ%
90.68	0.117	35.55	2.93	1.471	52.7	2095	212	-1.2	91.5	5.759	30.9	34.8	-11.2
100	0.345	36.55	3.11	1.745	54.3	1507	1530	-1.5	194.6	7.109	74.5	76.0	-1.9
110	0.884	37.76	3.38	2.145	55.6	1207	1200	0.6	273.1	8.423	106.4	102.6	3.7
120	1.919	39.13	3.74	2.710	56.9	1035	1040	-0.5	373.1	9.499	142.8	133.1	7.3
130	3.680	40.70	4.24	3.550	58.6	921	950	-3.1	473.7	10.849	176.7	160.5	10.1
140	6.419	42.54	4.93	4L830	61.0	838	750	11.7	557.1	11.954	202.7	181.3	11.8
150	10.40	44.78	5.97	6.980	65.0	775	665	16.5	653.1	13.196	230.4	202.6	13.7
									772.1	14.671	262.3	226.4	15.9

[a]Values taken from Ref. 10 [b]Values are the interpolated ones of Ref. 16 [c]Values taken from Ref. 5 p. 629 [d]Values taken from Ref. 12.

Table 5. Comparison of calculated and observed Viscosities of liquid and Gas for Carbon Tetrachloride

Liquid state									Gas state				
T K	P^a bar	V^a cm^{3}mol^{-1}	$10^3\alpha_p^a$ K^{-1}	$10^4\beta_T^a$ bar^{-1}	C_p^a JK^{-1}mol^{-1}	$\eta_{calc.}$ μP	$\eta_{obs.}^b$ μP	Δ%	T K	C_p^c cal mol^{-1}	$\eta_{calc.}$ μP	$\eta_{obs.}^d$ μP	Δ%
273	0.045	94.20	1.177	0.881	131.0	13206	13290	-0.6	350	21.11	109.9	—	—
283	0.075	95.33	1.198	0.954	131.3	9315	11100	-16.1	401	21.99	128.4	133.4	-3.7
293	0.122	96.49	1.220	1.032	131.7	7337	9690	-24.3	473	22.98	154.3	156.2	-1.2
303	0.189	97.68	1.241	1.117	132.0	6130	8430	-27.3	588	24.05	193.9	190.2	1.9
313	0.285	98.91	1.266	1.213	132.3	5317	7390	-28.1					
323	0.416	100.18	1.296	1.322	132.7	4731	6510	-27.3					
333	0.591	101.50	1.327	1.437	133.0	4280	5850	-26.8					
323	0.822	102.87	1.349	1.563	133.0	3932	5240	-24.9					
353	1.118	104.30	1.400	1.720	134.0	3656	4710	-22.4					

[a]Values taken from Ref. 10 [b]Values are the interpolated ones of Ref 16 [c]Values taken from Ref. 5 p. 629 [d]Values taken from Ref. 12.

Table 6. Comparison of calculated and observed Viscosities of liquid and Gas for Benzene

Liquid state									Gas state				
T K	P^a bar	V^a cm^{3}mol^{-1}	$10^3\alpha_p^a$ K^{-1}	$10^4\beta_T^a$ bar^{-1}	C_p^a JK^{-1}mol^{-1}	$\eta_{calc.}$ μP	$\eta_{obs.}^b$ μP	Δ%	T K	C_p^c cal mol^{-1}	$\eta_{calc.}$ μP	$\eta_{obs.}^d$ μP	Δ%
293	0.100	88.86	1.22	0.935	134.9	6533	6520	0.2	287.3	18.91	74.3	73.8	0.7
313	0.244	91.08	1.25	1.091	139.2	4720	5010	-5.8	404.3	27.05	112.0	103.1	8.6
333	0.522	93.46	1.29	1.281	144.3	3784	3920	-3.5	467.7	30.87	132.0	119.8	10.2
353	1.010	95.90	1.35	1.520	149.0	3264	3210	1.7	525.6	34.02	149.9	134.3	11.6
									585.9	36.97	168.1	148.4	13.3

[a]Values taken from Ref. 10 [b]Values are the interpolated ones of Ref. 16 [c]Values taken from Ref. 5 p. 629 [d]Values taken from Ref. 12.

Table 7. Comparison of calculated and observed Viscosities of liquid and Gas for Carbon Disulbide

Liquid state								Gas state				
T K	V^a cm^{3}mol^{-1}	$10^3\alpha_p^a$ K^{-1}	$10^4\beta_T^a$ atm^{-1}	C_p^a cal mol^{-1}	$\eta_{calc.}$ μP	$\eta_{obs.}^b$ μP	Δ%	T K	C_p^c cal mol^{-1}	$\eta_{calc.}$ μP	$\eta_{obs.}^d$ μP	Δ%
233	56.21	1.104	0.620	17.10	8751	—		273.1	10.62	100.4	91.1	10.2
273	58.94	1.155	0.814	42.74	4274	4360	- 1.9	387.4	11.70	151.1	130.3	15.9
313	61.70	1.211	1.065	18.50	3237	3301	-1.9	463.3	12.25	184.0	156.1	17.9
								582.9	12.91	134.0	196.6	19.0

[a]Values taken from Ref. 11 [b]Values taken from Ref. 14 [c]Values are the interpolated ones of Ref. 14 [d]Values taken from Ref. 12 [e]Values taken from Ref. 5 p. 629.

Table 8. Comparison of calculated and observed Viscosities of liquid and Gas for Acetone

Liquid state								Gas state				
T K	V^a cm^3mol^{-1}	$10^3\alpha_p^b$ K^{-1}	$10^4\beta_T^c$ atm^{-1}	C_p^b $cal\ mol^{-1}$	$\eta_{calc.}$ μP	$\eta_{obs.}^c$ μP	Δ %	T K	C_p^d $cal\ mol^{-1}$	$\eta_{calc.}$ μP	$\eta_{obs.}^c$ μP	Δ%
283	72.48	1.350	1.132	29.62	3698	3680	0.5	373.1	20.81	92.8	93.1	-0.2
293	73.43	1.375	1.229	32.23	3263	-1.3		463.5	24.41	118.4	118.6	-0.2
303	74.43	1.433	1.334	30.32	2935	2950	-0.5	520.8	26.49	134.2	133.4	0.6
313	75.48	1.463	1.464	30.72	2606	2800	-3.4	579.5	28.48	150.1	148.1	1.4
323	76.58	1.500	1.603	31.19	2472	2560	-3.4					

[a]Values taken from Ref. 11 [b]Values taken from Ref. 14 [c]Values taken from Ref. 12 [d]Values taken from Ref. 5 p. 629.

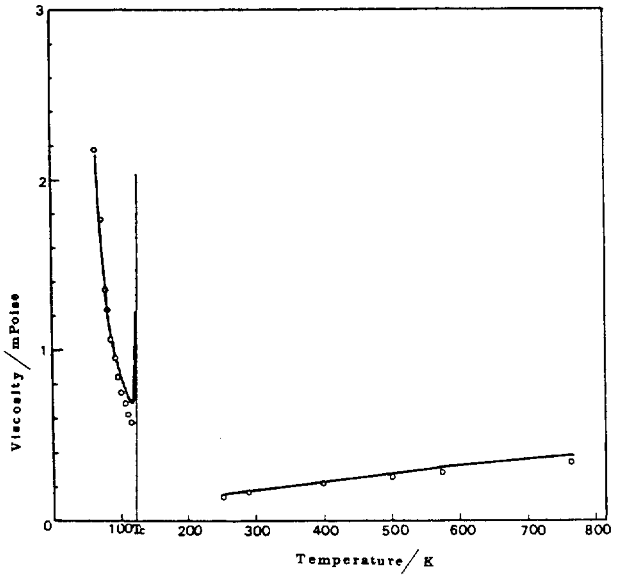

Figure 1. Viscosity of nitrogen for gas and liquid Solid line; Calculated, Open circles; Observed (from Ref. 16).

the observed molecular collision diameters instead of the ones for the phonons. The parametric value of V_s are the one obtained by fitting the calculated viscosity to the observed one at a temperature (for example, at the melting temperature). The obtained values of V_s are slightly higher than those of solid volumes.

Notwithstanding the use of the simple viscosity equation, the calculated viscosities are in excellent agreements with those of the observed ones for various fluids in both phases of liquid and gas.

The viscosity of gas is a strong function of pressure only in certain regions of pressure and temperature. Usually, pressure variations are not significant at very high temperatures or low pressures and $d\eta/dT > 0$ in these regions. At somewhat high pressures, the viscosity would be expected to increase sharply, and we see that there is a wide range of temperature where decreases with temperature. In this region, the viscosity behavior simulates more closely the liquid state one.

There is few theories to explain the effect of pressure on the viscosity of gas except Enskog theory[5]. But the Enskog equation can usually illustrate the dense gas viscosity only if the experimental data about the radial distribution function are available. In Figure 2, the calculated viscosities for nitrogen using a simple equation of state

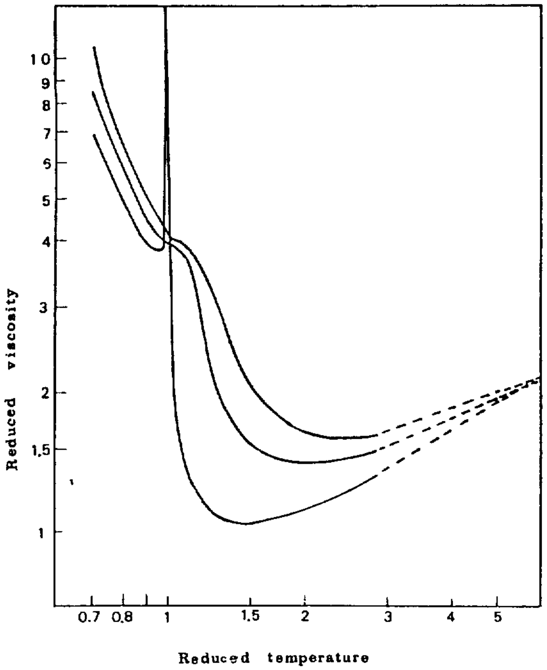

Figure 2. Viscosity of nitrogen for several values of reduced pressures by using eqs 9 and 12. $\eta_c = 61.6(MTc)^{1/2}\cdot(Vc)^{-2/3}$ (Ref. 17) C_p values are taken from Ref. 15. The parameters for nitrogen in eq. 12 are as follows; a; 3.03×10^5 atm. $(cm^3)^n$ b; $24.05cm^3$ n; 1.74.

$$P = RT/(V-b) - a/V^n \tag{12}$$

are shown, *a*, *b* and *n* being the parameters. It is clear that in the vicinity of the critical point pressure effects are quite important. At very high temperatures, there results a condition where there is but little effect of pressure on gas viscosity, and the viscosity is expressed as a simple form similar to the Maxwell viscosity equation as

$$\eta = \sqrt{2}\cdot\gamma^{-1/2}\cdot\eta_{Max} \tag{13}$$

where η_{Max} is the Maxwell viscosity.

The viscosity of fluid exhibits an anomalous enhancement near the gas-liquid critical region[6], and the experimental evidences[6] indicate that the shear viscosity diverges at the critical point. No general viscosity equation, however, has predicted the anomalous behavior. Some dicoupled theories[7,8] had been applied to the critical viscosity with little success. In Figure 3, we can exhibit the anomalous behavior slightly above the critical temperature. We can also find the divergence of viscosity at the critical point in Figures 1 and

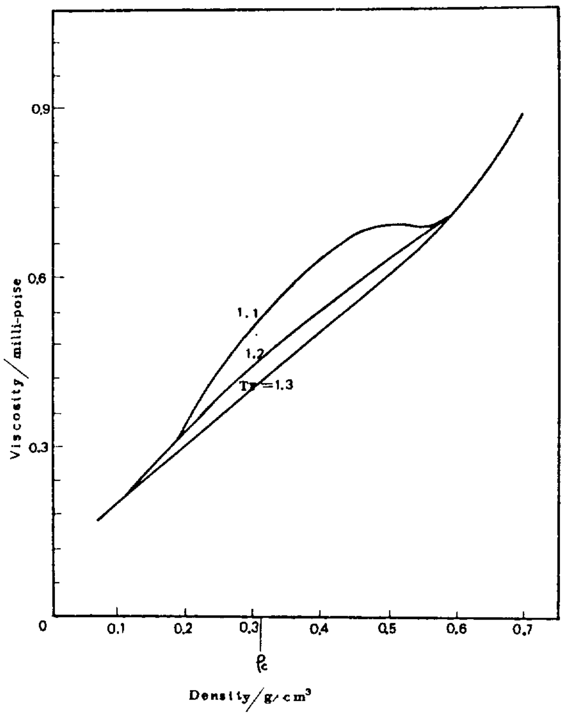

Figure 3. Viscosity of nitrogen at the temperature slightly above the critical temperature by using the same equations and the same parameters of Figure 2.

2. These behaviors are mainly because of the large compressibility near the critical point. We hope our viscosity equation is useful to explain the true nature of fluids.

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