monolayer surfactant. Therefore, in order to consider the effect of the anisotropy, we must use more refined approximation by which both energetic and entropic contributions to free energy are well described. In the future, by introducing the chain anisotropy in our approximation, we will study more general behavior of terminally anchored chain molecules.

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A Calculation for the Viscosity of Liquid Metals

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A phenomenological theory of viscosity which has been proposed by authors is applied to liquid metals for which the calculation is a severe test for liquid theories. The thermodynamic properties used in the calculations can be obtained by using the Roulette liquid theory. The calculated values of the viscosities for liquid metals are in good agreements with the observed values.

Introduction

The viscosities of liquid metals play an important role in liquid metal processing operation. Interests in the viscosity of liquid metals today stem from practical consideration, such as their use as atomic reactor coolants and from philosophical consideration, such as the fact that their structural simplicity makes them good media to test the current theories of the liquid state.

For liquid metals low pressures at melting, small differances in volume between liquid and solid, and rather large temperature ranges of the liquid state can lead to large differances between observed and calculated values for thermodynamic properties. Viscosity data[1] indicate that the hole size in metal melts is small relative to the size of metal stom

but is comparable to the volume of metal ion differantly from other liquids. Therefore the calculation for liquid metals is a severe test for liquid theories.

Among the current theories used in the calculation of the viscosity of liquid metals, the model theories of Andrade[2] and Eyring[3] have been often used. Their equations for the viscosity of liquid metals have proved to be useful for the calculation of the viscosity, but they have adjustable parameters and exponential form which is not physically meaningful.

A phenomenological theory[4] of viscosity which was proposed by authors had been sucessfully applied to normal liquid, water[5] and helium[6] which exhibits abnormal behavior compared to other ordinary liquids. This theory also can be used in the form of the reduced equation[7] because it does not

have any adjustable parameters. In this paper we apply this theory to liquid metals adequately as shown in other liquids.

Theory

According to the Maxwell theory[8] of the viscosity in liquids, the shear viscosity η is given by

$$\eta = \tau K' \tag{1}$$

where τ is the shear relaxation time and k' is the shear elasticity. But the relaxation frequency is far from measurements, and could not be obtained by using the theories of liquids. Therefore, it had not been applied to liquid viscosity for practical use. If we can find the values of τ and K' from other liquid theories, we can make use of the Maxwell theory for the calculation of the viscosity of liquids. If we assume that the relaxation time is the collision time for the phonon to collide each other and the shear elasticity is the absolute pressure, we can get the equation as the same as our viscosity equation.[4] As was shown in our equation, the collision time τ of the phonon, which propagates with a veloity V_{ph} and a mean free path λ_{ph}, is expressed as follows

$$\tau = \frac{\lambda_{ph}}{V_{ph}} = \frac{(\pi d^2 N_{ph})^{-1}}{(\gamma/\rho\beta_T)^{1/2}} \tag{2}$$

where N_{ph} is the phonon number density, ρ the liquid density, β_T the isothermal compressibility and γ the heat capacity ratio, Cp/Cv. The absolute pressure P_a^θ(kinetic pressure P_k + internal pressure P_i) is expressed as follows

$$P_a = P_k + P_i = T(\frac{\partial P}{\partial T})_v + \{(T\frac{\partial P}{\partial T})_v - P\} = 2T\frac{\alpha_P}{\beta_T} - P \tag{3}$$

where α_p is the isobaric thermal expansion coefficient and P is the pressure. Therefore we have

$$\eta = (\rho\beta_T/\gamma)^{1/2}(\pi d^2 N_{ph})^{-1}(2T\frac{\alpha_P}{\beta_T} - P) \tag{4}$$

When the temperature rises, the collision diameter, d, of the phonon must be expanded, then

$$d = d^\circ (1 + aT) \tag{5}$$

where d° is the collision diameter at O K and a is the linear expansion coefficient, respectively.

Calculation and Result

For the calculation of the viscosity of liquid metals by us-

ing eq.(4), we have to know the thermodynamic properties such as α_p, β_T and γ. For the liquid metals the experimental values of such properties have not been known because of their experimental difficulties. If we use the equation of state of liquid metals, we can find the various thermodynamic properties.

According to the Roulette theory[10] of liquid, the partition function of liquid Q is expressed as follow

$$Q = (q_s + q_c)^N \exp(\frac{q_g}{q_s + q_c}) \tag{6}$$

where q_s is the partition function for the solid-like molecules, q_c is the partition function for the cell-like molecules, q_g is the partition function for the gas-like molecules and N is the Avogadro's number, respectively. They are given by,

$$q_s = (1 - e^{-\theta/T})e^{E_s/RT} \tag{7}$$

$$q_c = (\frac{2\pi mkT}{h})^{3/2} \frac{(V - V_s)}{N} e^{E_c/RT} \tag{8}$$

$$q_g = (\frac{2\pi mkT}{h})^{3/2}(V - V_s)e^{E_g/kT} \tag{9}$$

where E_s and V_s are the ground state energy and the molar volume of solid-like molecule, E_c and E_g are the potential energy of the cell-like molecule and gas-like molecule as follows

$$E_c = a/X^n \tag{10}$$

$$E_s = E + E_c \tag{11}$$

$$E_g = E_g'/X^n T \tag{12}$$

where X is $\frac{V}{V_s}$ and a, E_g', E and n are the parametric constants. The parametric values can be found by the use of the following equations

$$P = -(\frac{\partial A}{\partial V})_{T, N} \tag{13}$$

$$S = -(\frac{\partial A}{\partial T})_{V, N} \tag{14}$$

$$A + PV = A_g + PV_g \tag{15}$$

where A_g and V_g are the Helmboltz free energy and the molar volume of the vapor which is in thermal equilibrium with the liquid. By using eqs. (13), (14) and (15), we find the parametric values and calculate the various thermodynamic

Table 1. Parameters Used in the Calculation

	$a \times 10^{-3}$ (cal/mol)	$E_g \times 10^{-6}$ (cal/mol.K)	n	E (cal/mol)	V_s^3 (cm³/mol)	θ^3 (K)	$d^{\circ a}$ (Å)	$a \times 10^4$ (K⁻¹)
Potassium	20.21	3.67	0.502	755	47.1	75.0	4.76	6.42
Rubidium	17.97	2.88	0.461	620	55.8	43.5	5.04	2.82
Cesium	17.45	4.035	0.462	964	70.0	31.5	5.40	10.79
Mercury	14.12	3.003	0.860	680	14.1	60.0	3.10	31.38
Lead	45.99	7.40	0.455	791	18.8	56.2	3.50	4.97

^{a}from ref. 17.

Table 2. Calculated Thermodynamic Properties of Potassium

T (K)	V (cm³/mol)	$\alpha_p \times 10^4$ (K⁻¹)		$\beta_T \times 10^5$ (atm⁻¹)		C_p (cal/K.mol)		C_v (cal/K.mol)	
		Calc.	Obs.[a]	Calc.	Obs.[a]	Calc.	Obs[a]	Calc.	Obs.[a]
342.9	49.704	2.203	(2.90)	0.938	(4.02)	5.83	(7.67)	3.69	(6.9)
440.4	50.771	2.174	—	1.302	—	5.56	—	3.60	
523.0	51.697	2.210	—	1.654	—	5.51	—	3.58	
623.0	52.874	2.291	—	2.147	—	5.53	—	3.58	
923.0	56.938	2.688	—	4.242	—	5.77		3.61	

[a]from ref. 15 and 16.

Table 3. Calculated Thermodynamic Properties of Rubidium

T (K)	V (cm³/mol)	$\alpha_p \times 10^4$ (K⁻¹)		$\beta_T \times 10^5$ (atm⁻¹)		C_p (cal/K.mol)		C_v (cal/K.mol)	
		Calc.	Obs.[a]	Calc.	Obs.[a]	Calc.	Obs[a]	Calc.	Obs.[a]
311.0	59.491	2.643	3.4	1.572	4.9	5.59	7.5	3.59	6.7
323.0	59.649	2.620	—	1.628	—	5.56	—	5.39	—
371.7	60.415	2.633	—	1.960	—	5.49	—	3.57	—
413.5	61.080	2.659	—	2.264	—	5.47	—	3.56	—
493.1	62.427	2.755	—	2.936	—	5.49	—	3.56	—

[a]from ref. 15 and 16.

Table 4. Calculated Thermodynamic Properties of Mercury

T (K)	V (cm³/mol)	$\alpha_p \times 10^4$ (K⁻¹)		$\beta_T \times 10^5$ (atm⁻¹)		C_p (cal/K.mol)		C_v (cal/K.mol)	
		Calc.	Obs.[a]	Calc.	Obs.[a]	Calc.	Obs[a]	Calc.	Obs.[a]
316.4	73.882	3.027	(3.7)	2.060	(6.73)	6.71	7.6	4.19	6.7
371.6	75.095	2.895	—	2.588	—	6.05	—	3.84	—
413.5	76.010	2.866	—	2.973	—	5.86	—	3.76	—
441.0	76.610	2.865	—	3.261	—	5.79	—	3.73	—
483.9	77.555	2.882	—	3.737	—	5.72	—	3.70	

[a]from ref. 15 and 16.

Table 5. Calculated Thermodynamic Properties of Mercury

T (K)	V (cm³/mol)	$\alpha_p \times 10^4$ (K⁻¹)		$\beta_T \times 10^5$ (atm⁻¹)		C_p (cal/K.mol)		C_v (cal/K.mol)	
		Calc.	Obs.[a]	Calc.	Obs.[a]	Calc.	Obs[a]	Calc.	Obs.[a]
253.0	14.642	1.779	—	1.401	—	13.78	6.73	11.75	—
273.0	14.696	1.846	1.81	1.536	3.80	7.14	6.7	4.98	5.44
293.0	14.750	1.851	—	1.674	3.95	5.99	6.67	3.84	—
373.0	14.971	1.868	—	2.287	—	5.46	6.58	3.40	—

[a]from ref. 15 and 16.

properties for liquid metals. The parameters are listed in Table 1 and the thermodynamic properties used in the calculation for the viscosity are listed in Tables 2 through 6. By using eq. (4) with the thermodynamic properties we have obtained the values of the viscosity of liquid metals. In Table 7, the calculated viscosities of potassium, cesium, rubidium, lead and mercury are compared with those of the observed values.

Discussion

Viscosities of liquid metals with few adjustable parameters are calculated by using the thermodynamic properties from Roulette liquid theory. The agreements between the calculated and observed values are resonably good.

Some theories[11-13] of viscosity have applied to liquid metals, but none of these theories provide satisfactory

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Table 6. Calculated Thermodynamic Properties of Lead

T (K)	V (cm^3/mol)	$\alpha_p \times 10^4$ (K^{-1})		$\beta_T \times 10^5$ (atm^{-1})		C_p (cal/K.mol)		C_v (cal/K.mol)	
		Calc.	Obs.[a]	Calc.	Obs.[a]	Calc.	Obs[a]	Calc.	Obs.[a]
729.0	19.992	0.941	1.3	1.887	2.9	5.31	7.25	3.65	5.6
842.0	20.207	0.952	—	2.267	—	5.32	—	3.67	—
976.0	20.469	0.970	—	2.756	—	5.35	—	3.69	—
117.0	20.754	0.993	—	3.320	—	5.39	—	3.72	—

[a]from ref. 15 and 16.

Table 7. Calculated Viscosities of Various Liquid Metals

	T (K)	η calc. (μpoise)	η obs.[a] (μpoise)	Δ %
Potassium	342.9	5150	5150	0.00
	440.4	3078	3310	12.02
	523.0	3011	2580	16.71
	623.0	2443	1910	27.91
	923.0	1504	1360	10.59
Cesium	316.4	6300	6299	0.00
	371.6	4582	4753	-3.59
	413.5	3814	4065	-6.17
	441.0	3437	3750	-8.34
	483.9	2975	3430	-3.27
Rubidium	311.0	6707	6734	-0.40
	320.9	6485	6258	3.62
	371.7	5682	4844	21.01
	413.5	5170	4133	25.09
	493.1	4435	3234	37.14
Lead	729.0	20673	21160	-2.30
	842.0	17544	17000	3.20
	976.0	14744	13490	9.30
	1117.0	12503	11850	5.51
Mercury	253.0	18450	18500	-0.27
	273.0	15200	16800	-9.52
	293.0	12904	15500	-16.75
	373.0	8233	12700	-35.17
	473.0	5372	10100	-46.81

[a]from ref. 3.

results. According to the significant structure theory which has been widely used for many liquids, the large deviations[14] were shown for the calculation of viscosities of liquid metals. As were shown in Tables 2 through 6, the calculated thermodynamic properties are not satisfactory compared with the observed values, because they have been obtained

through second derivatives. As some deviations occur in the calculated thermodynamic properties, the values of calculated viscosities are not in good agreements as those might be hoped. But it is clear that this theory is not incorrect, in principle, for liquid metals including many liquids to which we apply this calculated values for practical use.

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