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A Phenomenological Theory of Viscosities of Liquids†

Hiroshi KIHARA*, Ikuo OKAMOTO and Takamichi IIDA*****

Abstract

When melting point is approached from higher temperature, certain melts show an increase of viscosity considerably greater than the usual exponential temperature (for example, monatomic liquid metals). A model exists in which this feature is attributed to cluster formation.

In this paper, at first we have introduced the outline of the phenomenological theory of the viscosity of monatomic liquid metals by S. Takeuchi and T. Iida. By extending this theory, we have drived an expression for the viscosity of liquids with large temperature dependence. Namely, this is the generalization of already obtained theory, based on Einstein model and momentum transfer taking place at every extreme displacement.

Cluster shapes (spherical particles or non-spherical particles) and the temperature dependence of the average mass of clusters in a melt can be estimated semi-quantitatively by this expression.

1. Introduction

The strength of welds depends on the diffusion of the reacting species in the molten pool and the transfer of the species across the molten pool-base metal interface, so the viscosity and the surface tension of the melts are of considerably importance. From this point of view, as the basic research for the welding phenomena, we have studied theoretically and experimentally on viscosities, being sensitive to the structure of liquids.

Andrade[1] and Eyring[2] have developed a theory of rate processes based on a cell model of the liquid state and drived an expression for the viscus flow of monatomic liquids. However, the activation energy playing an important role in their theory is experimentally evaluated while its phyical meaning is unclear. On the other hand, making use of extensions of nonequibbrium statistical mechamics, Born and Green,[3] and Kirkwood and coworkers[4] have presented a molecular theory of viscosity in liquids. It should be noted that the equations are as a function of the intermolecular potential and the equilibrium radial distribution function g (r). However, at the present time, it is not possible to calculate the velocity correlation function by a rigorous method because of the lack in nonequilibrium statistical mechanics. The intermolecular potential also is not accurately known. Consequently, the agreement between calculated values and experimental values are not necessarily satisfactory. Furthermore the mathematical treatments of the equations are very complicated.

Then, aside from the phenomenological treatment based on the theories and experiments of liquids, S. Takeuchi and T. Iida[5] have drived an expression for the viscosity of monatomic liquid metals, on the assumptions that all equivalent harmonic oscillators, namely all atoms, have the same frequency (Einstein model) and momentum transfer takes place at every extreme displacement of each atom, by contacting with the atoms in neighboring layers.

Slags, molten salts and alloys show an increase of viscosity considerably greater than monatomic liquid metals, when melting point is approached from higher temperature. A model exists in which this feature is attributed to cluster formation. However, Cluster shapes and the temperature dependence of clustering can not be estimated quantitatively.

The present paper will introduce a treatment of the viscosity of monatomic liquids by S. Takeuchi and T. Iida and, based on their theory, will present an attempt to place cluster formation on a quantitative basis.

2. A phenomenological treatment of viscosity of liquids with large temperature dependence.

For transport coefficients (the coefficients of viscosity, diffusion and thermal conductivity) the calculation proceeds via a detailed molecular dynamics method. Such a calculation may be accomplished in one of two; either the equations of motion for each atom may be written down and solved continously on a large computer, or a model for the liquid may be assumed and the dynamical consequences of the model worked out. But the transport coefficients are integrals over all time. These integrals can not be expressed in a simple way in terms of the pair potential and pair distribution functions. For example, the Born

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and Green method involving the partially integrated Liouville equation does not lead to usefull result because of the lack of irreversibility in the Liouville equation.

Consequently, we consider that progress in understanding the transport coefficients depends upon phenomenological analysis.

2. 1 A phenomenological theory of viscosity of pure liquid metals by S. Takeuchi and T. Iida.

This method to viscosity calculations is based on models of the dynamical behaviour and the mechanism of the viscosity of liquid metals. Let us consider on the basis of experimental results as follows; both solid and liquid metals on either side of melting point have values similar to heat capacities for the harmonic oscillator, and have values similar to dispersion curves according to inelastic scattering of neutrons by phonons. Consequently, a solid-like model is possible at a high density liquid. In the case of Einstein model, that is, all atoms vibrate as independent harmonic oscillators, correct results are obtained in the high density. Of course, one of the basic phenomenon occuring in a liquid, namely, the allowed motion of a single atom must be concerned. Diffusion rate of $\sim 10^{-5}$ cm^2/sec are characteristic of liquid state. As compared to diffusion in the solid state, this represents a rapid motion, but on a gaseous picture it is slow. In order to discuss this phenomenon, it will be assumed that the motion of atoms is a cyclic process. Namely, we assume that an atom remains at a given site for a time. During this time it may vibrate about a centre of equilibrium position. After the elape of time, it is assumed that the atom moves freely and rapidly. At this stage, we will introduce a concept being proportional to the probability of an atom remaining at a given site, or the lifetime at a given site.

Assuming that the phenomena of viscosity of liquid metals is based on momentum transfer to make the mass velocity uniform. Supposing that the momentum transfer takes place at every extreme displacement, that is, temporary unions of atoms take place instead of collision with neighbours by vibrational atomic motion. In this way, the momentum is transported in the presence of the velocity gradient. We assume that the momentum transfer by free translational motion can be neglected.

Now, we begin by discussing the motion in a liquid in which the mass velocity varies from point to point. At the particular point considered, let us choose our axes so that the mass-velocity is parallel to the axis of x, while the surfaces of equal velocity are parallel to the plane of xy, thus in the neighbouthood of the point the mass-velocity is a function of z only. We suppose that the average value of the momentum of any single atom increases as z increases, that the planes z=constant are horizontal and that z increases as we move upwards. Consider the momentum transport for an atom which crosses the plane $z=z_0$, having a relative atom-velocity. If the atom (i) in its equilibium position, at the point away distance l from the plane $z=z_0$, vibrates with Einstein oscillator of a frequency ν inclined at an angle θ to the axis z, and contacts with atoms in neighbouring planes which are at a distance r away, the momentum transfer per unit time is

$$2\nu m_0 (dv/dz) r \cos\theta \tag{1}$$

where m_0 is the atomic mass, dv/dz the velocity gradient.

Since all directions of this atom-vibration may be regarded as equally probable, the probability of oscillating between θ and $\theta + d\theta$ is proportional to $\sin d\theta$.

i.e

$$2\times \frac{2\pi r \sin\theta \cdot r\, d\theta}{4\pi r^2} = \sin\theta d\theta \tag{2}$$

where, $\theta \leqq \cos^{-1} l/r$

The number of atoms between z=1 and z=1+dl planes per unit area is $\rho_0 dl$, wher ρ_0 is the average number of atoms per unit volume (number density). The number of atoms per unit solid angle at a distance between r and r+dr from the atom (i) is

$$\frac{4\pi r^2 \rho_0 g(r) dr}{4\pi} = r^2 \rho_0 g(r) dr. \tag{3}$$

On the other hand we must consider that the probability of the atom vibrating about a site, that is, the lifetime of the atom at each site; $P_0(\bar{T})$ ($\bar{T}$ is the thermalequilibrium temperature). Then, the total momentum transfer per unit time per unit area, namely, the viscus force per unit area becomes,

$$\begin{aligned} f=\frac{dp}{dt} &= \iiint 2\nu P_0(\mp) m_0 r \cos\theta \frac{dv}{dz} \cdot \\ &\times \rho_0 dl \sin\theta d\theta \cdot \rho_0 r^2 g(r) dr \\ &= 2\nu P_0(\mp) m_0 \rho_0^2 \frac{dv}{dz} \int_0^a r^3 g(r) \int dl \int_0^{\cos^{-1}\frac{l}{r}} \sin\theta\cos\theta d\theta \\ &= \frac{4}{3} \nu P_0(\mp) m_0 \rho_0^2 \frac{dv}{dz} \int_0^a g(r) r^4 dr \end{aligned} \tag{4}$$

where, a is the upper of the first peak in g (r). A few comments will be made on $P_0(\bar{T})$. When an atom gets kinetic energy equivalent to boiling point or more, we suppose that the atom can move freely from the vibrating state at a site to the translational motion. We assume that the probability of a thermal fluctuation

occuting is given as a Gaussian function, i. e

$$P_0(\mp)=1-\int_{T\geqq Tb}\sqrt{\frac{3}{8\pi}}\exp\left\{-\frac{3}{8}\left(\frac{T_b}{T}-1\right)^2\right\}d\left(\frac{T_b}{\mp}-1\right) \quad (5)$$

where, T_b is the boiling point (K).
From the eq. (4) and Newton's law for uniform viscus fluid ;

$$f=\eta\frac{dv}{dz} \quad (6)$$

finally, we obtain

$$\eta=\frac{4}{3}\nu P_0(\mp)m_0\rho_0^2\int_0^a g(r)r^4dr \quad (7)$$

Making an approximation with the radial distribution function at thermal equilibrium, the integration of g (r):

$$\int_0^a g(r)r^4dr\simeq\frac{2}{5}g(\sigma)\sigma^5 \quad (8)$$

is a fairly good approximation, where, σ is the average distance between the centers of atoms. Furthermore, using a relationship $\rho_0\sim 1/\sigma^3$ viscosity (η) is approximated by ;

$$\eta\simeq\frac{13}{25}\frac{m_0\nu}{\sigma}g(\sigma)P(\mp) \quad (9)$$

To calculate the equations (7) and (8), if the frequency ν is not known, we use Lindemann's formula[6] to first approximation. The formura is

$$\nu=C\sqrt{\frac{T_m}{MV^{\frac{2}{3}}}}$$

where ν is the fundamental frequency, T_m is the melting-point, M the atomic weight, V the volume of a gram-atom at temperature T_m, and the value of constant C is 2.8×10^{12}. By substituting the experimental values of viscosity, g (r), atomic mass (m), number density (ρ_0) and P_0 ($\mp$) into the equation (7), we can obtain the accurate value of the frequency (ν). Using the temperature variation of g (r) obtained experimentally, and supposing that the temperature dependence of the frequency can be neglected, the agreement between calculations and experiments for pure liquid metals is surprisingly satisfactory. For example, the calculated and observed values of lead and bismuth are shown in **Table 1.**

The obtained values of the frequency as before are 1.5×10^{12} for lead and 1.0×10^{12} for murcury.

On the other hand, the calculated values of the frequency from Lindemanns formular are 1.8×10^{12} and 1.2×10^{12} for lead and murcury, respectivery. Calculating from the structure factor, the frequency is 1.2×10^{12} for lead[7]. Their agreement is reasonable.

2.2 Thermodynamic and kinetic treatments of the viscosity of liquids with lalge temperature dependence.

Let us develope the phenomenological consideration of the viscosity of liquids with large temperature dependence, based on S. Takeuchi and T. Iida expression. Now, we will introduce an assumption as follows:

The strength of the interaction setween molecules (atoms) is a function of the distance between molecules (atoms) only. Namely, we assume that Einstein model holds if molecules exist at a distance more than a certain distance away, and if molecules exist within a certain distance, they form cluster by the strong interaction.

Consequently, if clusters exist in a liquid, in comparrison with mono-molecular liquids we must add more the viscus flow-energy needed to separate the molecules a certain deistance to Einstein model separation. Denoting the energy by θ_T, the kinetic energy needed to move a molecule from the vibrational state in a given site to the free translational motion must be $(T_b+\theta_T)$.

Then, in order to obtain θ_T, let us calculate thermodynamically the quantity of heat needed to expand a liquid unit volume at constant temperature. Where, we denote the quantity of heat by Q (cal/mol), the internal energy by U (cal/mol), the pressure by P (dyn/cm^2), the temperature by T ($^\circ$K), the molar volume by V (cm^3/mol) and the molar heat capacity by C (cal/mol. deg).

The mathematical formulation of the first low of thermodynamics for a hydrostatic system is

$$\delta Q=du+Pdv \quad (10)$$

U is a function of any two of P, V and T. Choosing T and V, we have

$$du=\left(\frac{\partial u}{\partial T}\right)_V dT+\left(\frac{\partial u}{\partial V}\right)_T dV \quad (11)$$

By eq. (10) and (11), the first law becomes

$$\delta Q=\left(\frac{\partial u}{\partial T}\right)_V dT+\left\{\left(\frac{\partial u}{\partial V}\right)_T+P\right\}dV \quad (12)$$

or, the molar heat capacity

$$C=\frac{\delta Q}{dT}=\left(\frac{\partial u}{\partial T}\right)_V+\left\{\left(\frac{\partial u}{\partial V}\right)_V+P\right\}\frac{dV}{dT} \quad (13)$$

This equation is true for any process involving any temperature change dT and any volume change dV.

From the definition of the specific heat at constant volume, $dV=0$

$$C_v=\left(\frac{\partial u}{\partial T}\right)_V \tag{14}$$

On substituting eq. (14) into eq. (13), we have

$$C=C_v+\left\{\left(\frac{\partial u}{\partial V}\right)_T+P\right\}\frac{dV}{dT} \tag{15}$$

On the other hand, the heat capacity, at constant volume, becomes from the eq. (15) as follows,

$$C_p=C_v+\left\{\left(\frac{\partial u}{\partial V}\right)_T+P\right\}\left(\frac{\partial V}{\partial T}\right)_P \tag{16}$$

Then, at constant volume, we have,

$$\left(\frac{\partial V}{\partial T}\right)_P=\frac{dV}{dT}=\alpha V \tag{17}$$

where, α is the volume expansivity.
Therefore, we get

$$\left(\frac{\partial V}{\partial T}\right)_V+P=\frac{C_p-C_v}{\alpha V} \tag{18}$$

At constant temperature ($dT=0$) we get from the eq. (12).

$$\frac{\delta Q}{dV}=\left(\frac{\partial u}{\partial V}\right)_T+P \tag{19}$$

Consequently, on combining equations (18) and (19), we obtain

$$\frac{\delta Q}{\partial V}=\frac{C_p-C_v}{\alpha V} \tag{20}$$

In this equation, $\delta Q/dv$ is the quantity of heat needed to expand unit volume for any substances at constant temperature. Then, the quantity of heat required to separate the distance between molecules away to the distance in which Einstein model holds, becomes

$$Q=\int_V^{V'}\frac{C_p-C_v}{\alpha V}dV \tag{21}$$

where, V' is the volume in which Einstein model holds. On substituting eq. (17) into eq. (21), we obtain

$$Q=\int_V^{V'}\frac{C_p-C_v}{\alpha V}dV=\int_V^{V'}\frac{C_p-C_v}{dv/dT}dV=\int_T^{T\eta=\eta_0}(C_p-C_v)dT \tag{22}$$

This is the equation transformed from the integration over volume into the integration over temperature.

Where, $T_{\eta=\eta_0}$ is the temperature in which Einstein model hold, then, $V=V'$. That is, transforming the quantity of heat energy into the unit in temperature and denoting the energy by θ_T, we get

$$\theta_T=k.Q=k\cdot\int_T^{T\eta=\eta_0}(C_p-C_v)dT \tag{23}$$

where, k is 0.504 (K·mol/cal) because 1 eV $=1.16\times10^4$ (K) $=2.305\times10^4$ (cal/mol).

Although the heat capacity at constant volume C is easily not measured, a simple thermodynamic relation connects C_v and C_p [8];

$$C_p-C_v=\frac{\alpha^2MT}{\beta\rho} \tag{24}$$

where, α is the volume expansivity

$$\alpha=\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

β is the compressibility at constant temperature

$$\beta=-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

M the molecular weight, and ρ density (g/cm^3).

Consequently, the values (C_p-C_v) can be calculated from the equation (24).

Therefore, in the liquid forming clusters, the probability of a molecule vibrating at a given site, i. e the lifetime of a molecule at each site becomes

$$P(\bar{T})=1-\int_{T\geq T_b}\sqrt{\frac{3}{8\pi}}\exp\left\{-\frac{3}{8}\left(\frac{T_b+\Theta_T}{\bar{T}}-1\right)^2\right\}\times d\left(\frac{T_b+\theta_T}{\bar{T}}-1\right) \tag{25}$$

On the other hand, we have assumed previously that clusters are formed if the intermolecular distance is within a certain distance. In this case, the average mass of particles in the liquid becomes larger than the mass of molecule. Denoting the average mass of the particles by m, the expression for the viscosity of liquids with large temperature dependence becomes approximately as follows,

$$\eta=\frac{4}{3}\nu P(\bar{T})m\rho_0^2\int_0^a g(r)r^4dr \tag{26}$$

This expression is the generalization of the already obtained theory by S. Takeuchi and T. Iida. If viscosities are measured we can calculate the average mass of the particles (m) from this equation. The θ or P ($\bar{T}$) is considered to be a parameter meaning the strength of the interaction between molecules.

Consequently, cluster shapes (sphericul particles or non-spherical particles) and the temperature dependence of the average mass of clusters can be estimated by this equation. The comparison of the calculated results with experimental results are summarized in **Table 1—2.**

3. Summary

As the basic reseach for the welding phenomena, we have studied on the viscosities of melts.

Table 1. Comparison of experimental values of viscosity for lead and bismuth with values calculated on eq. (26).

Temperature (°C)	(°K)	P (∓)	bisumuth (g/cm³)	η cal. ($_c$p)	η exp. ($_c$p)
1000	1273	0.672	9.19	0.8	0.8
700	973	0.728	9.56	1.0	1.0
500	773	0.810	9.79	1.1	1.1
400	673	0.868	9.91	1.3	1.3
300	573	0.930	10.03	1.4	1.5
271	544	0.946	10.07*	1.5	1.6*
		lead			
1000	1273	0.695	9.84	1.1	1.1
700	973	0.773	10.21	1.4	1.4
500	773	0.868	10.46	1.8	1.8
400	673	0.922	10.59	2.2	2.2
327	600	0.956	10.68*	2.5	2.6*

*Extrapolated values.

Table 2. The values of η and m/m. for benzen, carbon tetrachloride and methanol.

Temperature (°C)	(°K)	P_o(∓)	θ_T (°K)	P (∓)	η_o (cP)	η exp (cP)	η exp / η_o	m / m_o
				benzen				
78	351	0.655	0	0.655	0.323	0.323*	1.00	1.0
60	333	0.655	81	0.666	0.347	0.388	1.12	1.1
40	313	0.656	178	0.711	0.378	0.487	1.29	1.1
20	293	0.660	261	0.779	0.411	0.640	1.56	1.2
5.5	279	0.663	324	0.838	0.439	0.810*	1.85	1.3
				carbon tetrachloride				
77	350	0.655	0	0.655	0.495	0.495*	1.00	1.0
50	323	0.655	129	0.683	0.556	0.648	1.17	1.1
20	293	0.659	273	0.784	0.624	0.954	1.53	1.3
0	273	0.665	368	0.872	0.695	1.32	1.91	1.5
−22	251	0.674	473	0.951	0.800	2.08*	2.59	1.8
				methanol				
60	333	0.655	0	0.655	0.345	0.345*	1.00	1.0
50	323	0.655	18	0.655	0.355	0.388	1.09	1.1
20	293	0.657	71	0.673	0.404	0.577	1.43	1.4
0	273	0.660	106	0.698	0.437	0.787	1.80	1.7
−20	253	0.667	142	0.742	0.485	1.11	2.29	2.1
−27.5	246	0.670	155	0.761	0.494	1.31*	2.66	2.3

*Extrapolated values

In the present paper, at the start we have introduced the outline of a phenomenological theory of viscosity of monatomic liquid metals by S.Takeuchi and T. Iida, based on Einstein model and momentum transfer taking place at every extreme displacement by contacting with neighbours.

By extending this theory, we have drived thermodynamically an expression for the viscosity of liquids with large temperature dependence, which is attributed to cluster formation.

Cluster shapes and the temperature dependence of clustering, that is, the temperature dependence of

the average mass of the clusters can be estimated semi-quantitatively by this expression.

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