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Viscosity, hard sphere diameter and interionic potential for liquid lead

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Résumé. — L'équation hybride de Macedo-Litovitz est utilisée conjointement avec un modèle *sphères dures* pour rendre compte de la viscosité du plomb entre $T = 600$ et $1\,400$ K. Une compacité de 0,472 au point de fusion ainsi qu'une variation linéaire du diamètre de cœur dur σ avec $T^{1/2}$ sont en très bon accord avec les résultats déduits de la théorie de Enskog et de la dynamique moléculaire. L'énergie d'activation : 0,07 eV trouvée est voisine de la hauteur de la barrière de potentiel interionique prévue à partir de l'équation de Percus-Yevick et des fonctions de corrélation déterminées par diffraction de neutrons.

Abstract. — The Macedo-Litovitz equation for a *hard sphere* liquid provides a satisfactory model for the viscosity of lead up to $1\,400$ K. The packing fraction at the melting point ($\zeta_m = 0.472$) and the $T^{1/2}$ temperature dependence of the hard core size σ are in good agreement with other results deduced from Enskog's theory and molecular dynamics. The activation energy for viscosity (0.07 eV) is similar to the height of the interionic potential barrier calculated from the correlation functions determined by means of neutron diffraction, and the Percus-Yevick theory.

1. **Introduction.** — Transport properties of high density liquids can be satisfactorily described in the framework of the hard sphere model by using a corrected Enskog's theory [1-3].

The hard core size σ is close to intermolecular distances obtained from neutron diffraction measurements [4, 5]. For liquid metals the temperature dependence of σ is simply correlated with the interionic potential as shown by Protopapas *et al.* [6-8].

A more phenomenological approach to transport properties in liquids is the *free volume* formalism [9-12]. Macedo-Litovitz [13] and Chung [14] have reconsidered this formalism and proposed an hybrid equation for viscosity by using simple considerations concerning the interionic potential barrier. Both theories [9, 10, 13, 14] are of great interest to account for the viscosity of non associated or associated liquids, such as glass forming liquids [15, 16] and polymers [13, 17, 18]. In this paper the Arrhenius behaviour of kinematic viscosity for pure lead is well described up to $1\,400$ K by a hard sphere model using both the Macedo-Litovitz equation and a temperature dependent hard core size σ . The values of σ and the height of the interionic potential barrier ε^* are in good agreement with the results derived from neutron diffraction data [19].

2. **Model.** — 2.1 INTERATOMIC POTENTIAL AND HARD CORE SIZE. — Figure 1 gives a schematic representation of interionic potential $\phi(r)$. The temperature dependence of σ is well described by eq. (1) assuming that $\phi(r)$ is parabolic near r_0 and kT is small [6] :

$$\sigma = \sigma_0 \left\{ 1 - B \left(\frac{T}{T_m} \right)^{1/2} \right\} \quad (1)$$

T_m melting temperature.

Fig. 1. — Schematic representation of the interionic potential $\phi(r)$ used in paragraph 2.1.

The hard sphere diameter σ is the average distance of closest approach for repulsive collisions in the fluid [6]. If $p(E) dE$ denotes the probability of finding an atom with energy in the interval $E, E + dE$, we can write in the classical limit and in the case of a parabolic well [14] :

$$p(E) dE = \left(\frac{1}{2kT} \right) \left(\frac{E}{kT} \right)^2 \exp \left(-\frac{E}{kT} \right) dE. \quad (2)$$

2.2 SELF-DIFFUSION COEFFICIENT. — If $p(v) dv$ is the probability of finding a free volume between v and $v + dv$ [9] :

$$p(v) dv = \left(\frac{\gamma}{v_F} \right) \exp \left\{ -\frac{\gamma v}{v_F} \right\} dv \quad (3)$$

v_F is the mean free volume and γ a coefficient, arbitrarily taken equal to unity.

Diffusion in liquids is governed by two simultaneous events :

- 1) The presence of an adjacent free volume of size greater than v^* .
- 2) The acquisition of energy surpassing a critical value ε^* by the diffusing atom.

The self-diffusion coefficient D given by Turnbull in reference [15] can be rewritten in the following manner :

$$D = \frac{1}{3} \frac{\gamma}{v_F} \bar{u} \alpha \frac{1}{2kT} \int_{v^*}^{\infty} \int_{\varepsilon^*}^{\infty} v p(E) dE p(v) dv \quad (4)$$

assuming : (i) The displacement a of an ion is a linear function $a = \alpha v$ of the free volume v , (ii) the ions move with the gas kinetic velocity $\bar{u}$.

By integrating eq. (4) gives :

$$D = \frac{1}{3} \gamma \bar{u} \alpha \left(v^* + \frac{v_F}{\gamma} \right) \left\{ \frac{1}{2} \left(\frac{\varepsilon^*}{kT} \right)^2 + \left(\frac{\varepsilon^*}{kT} \right) + 1 \right\} \times \exp \left\{ -\left\{ \frac{\gamma v^*}{v_F} + \frac{\varepsilon^*}{kT} \right\} \right\}. \quad (5)$$

Let ζ be the packing fraction of the hard sphere fluid. $\bar{v}_m$ denotes the mean molecular volume and $\bar{v}_{m0}$ is the value of $\bar{v}_m$ for $\zeta = \zeta_0 = 0.74$ (hard packing). Assuming $v_F = \bar{v}_m - \bar{v}_{m0}$ and $v^* = \bar{v}_{m0}$ eq. (5) is rewritten in the following form :

$$D = \frac{1}{18} \alpha \bar{u} \frac{\pi \sigma^3}{\zeta} \left\{ \frac{1}{2} \left(\frac{\varepsilon^*}{kT} \right)^2 + \left(\frac{\varepsilon^*}{kT} \right) + 1 \right\} \times \exp \left\{ -\left\{ \frac{\zeta}{\zeta_0 - \zeta} + \frac{\varepsilon^*}{kT} \right\} \right\}. \quad (6)$$

2.3 VISCOSITY. — For a hard sphere dilute gas [20] :

$$D = 1.019 \frac{3}{8n} \frac{1}{\sigma^2} \left(\frac{kT}{\pi m} \right)^{1/2}. \quad (7)$$

Eq. (7) is identical in the limit $\zeta \rightarrow 0$ and $\varepsilon^* \rightarrow 0$ to eq. (6). Then the value for α is : $0.4053/\sigma^2$.

The assumption $a = \alpha v$ is strictly valid only for dense fluids (if $v \rightarrow 0$), consequently this estimation for α is only a rough approximation.

For spherical molecules, the Stokes-Einstein relationship is valid :

$$\frac{\eta D \sigma}{kT} = C \quad (8)$$

where C is a constant. ($C = 1/2 \pi$ for liquid metals [7]) and η is the shear viscosity coefficient.

The kinematic viscosity is expressed by :

$$\nu = \frac{\eta}{d} = \frac{AT^{1/2}}{\left[1 + \left(\frac{\varepsilon^*}{kT} \right) + \frac{1}{2} \left(\frac{\varepsilon^*}{kT} \right)^2 \right]} \left(\frac{\zeta}{d} \right)^{1/2} \times \exp \left[\frac{\zeta}{\zeta_0 - \zeta} + \frac{\varepsilon^*}{kT} \right] \quad (9)$$

$A = 0.4065 \times 10^{-4}$ for lead, d is the density.

3. Results and discussion. — **3.1 RESULTS.** — The kinematic viscosity ν of liquid lead was measured with a Meyer Schvidkovskii torsional oscillating cup viscometer. The absolute value of ν was determined with an estimated error of 10 % but for the temperature dependence of the viscosity the relative precision is 2 %. In the range of measurements from melting point to 800 °C our results are similar to those in references [3] and [7] (Fig. 2).

Fig. 2. — Experimental values of kinematic viscosity ν for liquid lead as a function of $1/T$. The straight line corresponds to the Arrhenius law $\nu = \nu_0 \exp(W/kT)$ with an apparent activation energy $W = 0.07$ eV.

In figure 2 we plot $\log \nu$ versus $1/T$. Experimental ν values are also given in table I. The apparent activation energy of an Arrhenius law $\nu = \nu_0 \exp(W/kT)$ is $W = 0.07$ eV. ζ and σ were calculated from experimental values of ν and eq. (9). ε^* is an adjustable parameter. Taking $\varepsilon^* = 0.06$ eV and $\zeta = 0.465$ at

Table I. — ν_{exp} = experimental values of kinematic viscosity of figure 1; ν_{calc} = kinematic viscosity calculated with eq. (9); σ_{calc} = hard sphere diameter deduced from eq. (1); ζ = packing fraction used in eq. (9).

T (°C)	$\nu_{\text{exp}} = \nu_{\text{calc}}$ (cS)	ζ	σ (Å)	σ_{calc} (Å)	$\frac{\sigma - \sigma_{\text{calc}}}{\sigma} \times 10^3$
327	—	0.472 (*)	—	3.072 (*)	—
340	0.215	0.465	3.061	3.065	− 1.4
400	0.192	0.451	3.037	3.036	+ 0.5
450	0.174	0.438	3.014	3.012	+ 0.7
500	0.160	0.425	2.990	2.989	+ 0.3
550	0.150	0.414	2.970	2.967	+ 1.1
600	0.141	0.403	2.950	2.946	+ 1.5
650	0.132	0.390	2.924	2.925	− 0.2
700	0.127	0.381	2.908	2.905	+ 1.1
750	0.121	0.370	2.886	2.885	+ 0.3
800	0.116	0.360	2.866	2.866	0.0
850	0.111	0.348	2.840	2.847	− 2.5
900	0.108	0.339	2.821	2.828	− 2.6
950	0.105	0.331	2.805	2.810	− 1.9
1 000	0.103	0.323	2.788	2.793	− 1.5
1 050	0.101	0.316	2.774	2.775	− 0.4
1 100	0.100	0.310	2.763	2.758	+ 1.6
1 150	0.099	0.304	2.751	2.742	+ 3.5

(*) The packing fraction and the hard core size at the melting point are extrapolated.

340 °C the temperature dependence of σ agrees well with eq. (1) written in the following form :

$$\sigma_{\text{calc}} = 3.68 \left(1 - 0.166 \left(\frac{T}{600} \right)^{1/2} \right) \quad T_m = 600 \text{ K}.$$

As shown in table I, $(\sigma - \sigma_{\text{calc}})/\sigma$ does not exceed 0.25 % up to 1 100 °C. The variation of σ in the range of measurements is approximately 10 %, then the subsequent precision in the agreement with eq. (1) is about 2.5 %.

3.2 DISCUSSION. — Previously, using total and direct correlation functions obtained from neutron diffraction experiments North *et al.* [19] have calculated a Percus-Yevick interionic pair-potential. Assuming σ_0 is the position of the potential well and ϵ^* the height of the potential barrier our results are in very good agreement with [19].

By comparing σ with r_{max} , the first peak position of radial distribution function [19] as shown in

Table II. — σ = hard core diameter of table I; r_{max} = position of the first peak of the radial distribution function given by North *et al.* [19].

T (°C)	r_{max} (Å)	σ/r_{max}
340	3.40	0.90
600	3.32	0.89
780	3.30	0.87
1 100	3.23	0.86

table II we found 0.9 for σ/r_{max} at 340 °C. This value has been observed for other liquids and salts at the melting point [5], and considered as an indication of a relation between σ and mean spacing of short-range order.

The temperature dependence of σ is consistent with the hypothesis of paragraph 2.1 and reference [6].

The packing fraction $\zeta_m = 0.472$ at the melting temperature corresponds to the usual assumptions for liquid metals [6, 7, 21] and fits very well Lindemann's law [22, 23].

For B in eq. (1) Protopapas *et al.* [6] predicted a value equal to 0.112 for all metals, we found 0.166. The difference is about 50 % but only 6 % for σ_0 .

The precision $\Delta\zeta/\zeta$ on the calculated packing fraction which results from the experimental error $\Delta\nu/\nu = 10$ % mentioned above is 2 % at 340 °C and 6 % at 1 100 °C, but the corresponding precision $\Delta\sigma/\sigma$ is only 1/3 $\Delta\zeta/\zeta$. For a given value of ϵ^* the effects of $\Delta\nu/\nu$ on the preceding discussion are small : viscosity is very sensitive to variations of the hard core size. However, at 340 °C for the value $\zeta = 0.465$, the relative variation $\Delta\epsilon^*/\epsilon^*$ giving rise to $\Delta\nu/\nu = 10$ % is about 30 % : viscosity is less sensitive to variation of ϵ^* , if ϵ^* is small.

4. Conclusion. — The model gives a simple connection between viscosity and interionic pair potential. Both for non associated and associated liquids, viscosity measurements provide a practical method for investigating interatomic forces. For lead the agree-

ment with other observations is quite satisfactory and the ε^* and ζ_m values present some physical interest. However the choice of ε^* and ζ_m acting as

adjustable parameters for viscosity, is not sufficiently critical and must be completed with data given by other experiments such as neutron diffraction.

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