

A possible theoretical explanation to the gap dependence of the shear viscosity of thin liquid films under the transition regime

Máximo García-Sucre^{1,2*}, Germán Urbina-Villalba^{1,2}, Luis Lamedea³
and Rixio Parra¹

¹Centro de Física, Instituto Venezolano de Investigaciones Científicas (IVIC)

²Escuela de Química, Facultad de Ciencias, Universidad Central de Venezuela
Caracas, Venezuela.

³Departamento de Física, Universidad de Oriente, Cumaná, Edo. Sucre, Venezuela.

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Abstract

In this paper a simple relation, resulting from a Boltzmann equation treatment of the shear viscosity of gases in the Transition regime, has been applied to the case in which a fluid is sheared between two parallel plates at molecular separations. It was found that the application of this theory to the thin liquid film case results in agreement with the main features of the experimental data found for water, cyclohexane, and octamethylcyclsiloxane (OMCS). The most remarkable theoretical predictions been: (a) The occurrence of narrow regions of a periodic rapid variation of viscosity when the separation between the solid plates is varied. These narrow regions being separated by a distance ΔL of the order of the width of a monolayer (δ); and b) When δ is estimated from the density of the liquid, then our model predicts that $\Delta L/\delta$ is a constant near to unity (0.8032) for all liquids.

Key words: Oscillatory forces; thin liquid films; transition regime; viscosity.

Una posible explicación teórica para la dependencia de la viscosidad de películas líquidas delgadas en régimen de transición con la brecha de confinamiento

Resumen

En este trabajo una relación simple resultante de un tratamiento con la ecuación de Boltzmann de la viscosidad de gases en el régimen de Transición, es aplicada al caso en que un fluido es cortado tangencialmente entre dos placas paralelas a separaciones moleculares. Se encontró que la aplicación de esta teoría al caso de películas delgadas líquidas resulta en un acuerdo considerable con la data experimental medida para agua, ciclohexano, y octametil

* Autor para la correspondencia. IVIC, Centro de Física, Altos de Pipe, Carretera Panamericana, Km 11, Apdo. 21827, Caracas, Venezuela.

ciclosiloxano (OMCS). Nuestro modelo predice: a) La aparición de regiones periódicas de rápida variación de la viscosidad cuando se modifica la separación entre las placas sólidas. Estas regiones de variación rápida están separadas entre sí por una distancia ΔL del orden del ancho de una monocapa (δ); y b) Si δ es estimado a partir de la densidad del líquido, entonces nuestro modelo predice que $\Delta L/\delta$ es una constante cercana a la unidad (0.8032) para los líquidos.

Palabras clave: Fuerzas oscilatorias; películas líquidas delgadas; régimen de transición; viscosidad.

Introduction

A series of papers on a model for the shear viscosity of gases in the Transition regime, has been published by our group since 1978 [1-5]. In that approach, the Boltzmann equation was employed in order to calculate the tangential stress for a gas confined between two solid surfaces, keeping terms up to third order in the collision time. It was assumed that the local molecular distribution of velocities is Maxwellian, an assumption that has been experimentally confirmed even for the extremely dilute Knudsen regime [6], employing static and dynamic gas expansion techniques.

The fact that a transported quantity depends on density in a non monotonic way in the Transition regime, is determined in that model by three factors [4]: 1) The mathematical form of the equation of transport, which is a differential equation relating the flux (Ψ) of the transported quantity, say ϕ whose non uniform spatial distribution is related to the transport phenomena under consideration, i.e. $\Psi = F(\partial\phi/\partial z, \partial^3\phi/\partial z^3)$, where F is a linear function, and z is the direction along which the transport occurs; 2) The boundary values for ϕ and its spatial derivatives at the walls; and 3) The state in which the system is found in connection with its steadiness, which in our case includes the constancy of the flux Ψ of the transported quantity along z .

Within the referred model, it can be demonstrated [2], employing constant boundary conditions and assuming laminar flow, that the shear viscosity is a periodic function of the

density. The viscosity presents narrow regions of rapid variation that may correspond to either high or low values whenever:

$$\tan(\omega L/2) = \omega L/2 \quad [2]$$

$\omega = (\eta/\gamma)^{1/2}$ being the square root of the quotient between the first (η) and third order (γ) coefficients of the tangential stress (P_{zx}) in terms of the spatial derivatives of the fluid velocity (u_x):

$$P_{zx} = -\eta \frac{\partial u_x}{\partial z} - \gamma \frac{\partial^3 u_x}{\partial z^3} \quad [3]$$

where "x" is the direction of the fluid flow, and "z" is the axis parallel to the velocity gradient, $\eta = (\pi/8) mnvl$, and $\gamma = (3\pi/64) mnvl^3$, n being the gas density, m the molecular mass, v the molecular velocity, and l the mean free path of the gas molecules.

It can be deduced from Eq. 2 that the molecular cross section (σ) is related to the separation in density of the regions of non monotonic variation of the shear viscosity, Δn , according to [2-3]:

$$\sigma = \frac{1}{(4/3 \pi^3)^{1/2} \Delta n L} \quad [4]$$

where n is expressed in number of molecules per unit volume, and L is the distance between the relative moving plates of the system (viscometer).

In the usual Transition regime situation for gases, the pressure is diminished so that

the length of the mean free path is of the order of the size of the container. Therefore, the gas molecules have an approximately equal number of collisions with the walls of the container as they do with similar gas molecules. Thus, the non monotonic behavior of the shear viscosity of gases in the Transition regime, strongly depends on the structure of the walls. In this respect, this case (Case I) is *similar* to that case in which the shear viscosity of a fluid is measured employing an apparatus which restricts that fluid to wall separations of the size of the molecular mean free path (Case II). Both cases -by definition- belong to the Transition regime, but in Case I, the transmission of momentum between the molecules involves non local effects, since a fluid molecule travels a macroscopic length prior to the collision with either the wall or a similar molecule. In Case II however, the fluid molecules undergo several collisions before they reach the walls, so that non local effects are much less diminished, and instead, the behavior of the shear viscosity appears to be dominated by the possible geometric arrangements that those molecules can assume in the neighborhood of the walls.

Short range oscillatory solvating forces arise experimentally whenever liquid molecules are induced to order into quasi-discrete layers between two surfaces or within any highly restricted space [7]. It is now well established that [7-8]: (1) In liquids where molecules are roughly spherical and fairly rigid, the periodicity of the oscillatory force with respect to the distance between the confining surfaces is nearly equal to the width of a monolayer, which in turn can be considered approximately equal to the mean molecular diameter, d ; and (2) The peak to peak amplitude of the oscillations show a roughly exponential decay with distance, with a characteristic decay length of $1.2 d$ to $1.7 d$.

Measurements on the viscosity of thin liquid films by vibrating the upper curved mica surface of the SFA (Surface Forces Apparatus) showed [8], that when two surfaces are far apart than ten molecular diameters, a

simple liquid in the gap retains its bulk Newtonian behavior and the shear plane remains coincident with the physical solid-liquid interface. However, the use of a modified SFA with a lateral sliding mechanism specifically designed for viscosity measurements showed that [10], the viscosity of thin films less than 10 molecular diameters rises considerably [11]. In fact, when two molecularly smooth mica surfaces slide past each other with one or two layers of cyclohexane in between them, the "effective" shear viscosity is 5-7 orders of magnitude higher than the bulk value, and the molecular relaxation times can be 10^{10} times slower. The films exhibit a yield point and the shear stress no longer depends on the shear rate. The sliding now occurs with the surfaces separated by an integral number of liquid layers at surface separations coinciding roughly with the energy minimum of the oscillatory force curves, and the shear stresses are said to be "quantized" with the number of layers.

Results and Discussion

The use of Eq. 2 for the *comparable* hypothetical experiments in which the mean free path is kept fixed (and so the density), but the separation between the walls is continuously decreased leads to:

$$\Delta L = \frac{1}{(4/3 \pi^3)^{1/2} n \sigma} \quad [5]$$

where ΔL is the separation between regions of rapid variation of the shear viscosity when the distance L between the plates is varied.

Employing Eq. (5) for the same substances for which usual oscillatory force experiments had been made and assuming than the density of the thin films is approximately equal to that of the bulk liquids: water ($n_w = 0.33444 \times 10^{23}$ molec/cm³, diameter (d)= 1.69 Å), cyclohexane ($n_c = 0.05572 \times 10^{23}$ molec/cm³, $d = 5.5$ Å), octamethylcyclsiloxane ($n_{OMCS} = 0.019402 \times 10^{23}$ molec/cm³, $d = 8.5$ Å), one

finds that the oscillations caused by non local effect should appear at wall separations of 9.465, 1.656, and 1.287 monolayers for water, cyclohexane and OMCS, respectively. This appears to indicate, that the described phenomenon is not equal to that found by Israelachvili [7,8-10], but is rather complementary. However, if one calculates the mean cross section from the density of the liquids, i.e., supposing that the void spaces between molecules are ascribed to hard sphere volumes, then, the separation of the oscillations in terms of the "effective molecular diameter" d' comes out constant as we will now show. Note that when we estimate the width δ of a monolayer from the density of the liquid, i.e. $\delta = d'$, instead of equalizing δ with the hard sphere molecular diameter d , we are in a certain way taking into account the void spaces between molecules in the calculation of δ .

Let us estimate the molecular volume using:

$$\frac{4}{3} \pi \left(\frac{d'}{2}\right)^3 = v_1 \quad [6]$$

where d' is the effective molecular diameter and v_1 the molecular volume which can be directly obtained from the density according to:

$$v_1 = \frac{1}{n} = \frac{MW}{d_1 N_0} \quad [7]$$

where n is the number of molecules per unit volume, MW is the molecular weight of the substance, d_1 is the density of the liquid under consideration, and N_0 Avogadro's number. Equalizing Eqs. 6 and 7 it is found that the effective molecular diameter gives:

$$\frac{1}{n} = \frac{4}{3} \pi \left(\frac{d'}{2}\right)^3 \implies d' = \left(\frac{6}{\pi n}\right)^{1/3} \quad [8]$$

The effective molecular cross section can then be estimated as:

$$\sigma = \pi \left(\frac{6}{\pi n}\right)^{2/3} \quad [9]$$

Finally, introducing Eqs. 8 and 9 into Eq. 5, one finds:

$$\Delta L/d' = \frac{1}{\left(\frac{4}{3\pi^3}\right)^{1/2} n \left[\pi \left(\frac{6}{\pi n}\right)^{2/3}\right] \left(\frac{6}{\pi n}\right)^{1/3}} = \frac{1}{6 \left(\frac{4}{3\pi^3}\right)^{1/2}} = 0.8037 \quad [10]$$

Curiously enough, the gap between the oscillations comes out to be constant, of the order of 0.8037 monolayers, i.e., almost one monolayer as experimentally found.

Conclusions

From the results, it appears that the theoretical model developed by Garcia-Sucre and Moronta in 1982 for the Transition regime case, is able to account for the oscillation of the force between two mica surfaces separated by a thin liquid film. Still, modifications due to the curvatures of the supposedly planar confining surfaces are expected [5, 12]. As a further development of the results presented here, a more elaborate model for the Transition regime, which takes into account essential features of liquids, should be considered for the analysis of this effect.

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