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N. JHUNJHUNWALA
J. P. BOON, H. L. FRISCH
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J. L. LEBOWITZ

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THE SHEAR VISCOSITY OF SIMPLE FLUID MIXTURES

N. JHUNJHUNWALA* ‡‡

Belfer Graduate School of Science, Yeshiva University, New York, New York, USA,

J. P. BOON**, H. L. FRISCH‡,

Bell Telephone Laboratories, Murray Hill, New Jersey, USA

and

J. L. LEBOWITZ‡‡

Belfer Graduate School of Science, Yeshiva University, New York, New York, USA

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Synopsis

In this paper we present a simple model for the shear viscosity of simple liquid mixtures, based on the Enskog-Thorne theory. Numerical computations for the argon-krypton system lead to very good agreement with experimental data.

1. *Introduction.* Available experimental data on the transport properties of simple liquid mixtures are scarce[1]). Some of the results have been interpreted theoretically and quite good agreement is obtained, in particular, with the predictions of the liquid transport theory of Rice and co-workers[1,2]). We ask to what extent we can represent the experimentally observed viscosity of a simple liquid system (namely, the argon-krypton mixture) as the viscosity of a hypothetical, dense, hard-sphere fluid undergoing independent binary collisions, as envisioned in the Thorne extension of the Enskog theory[3]), with contact radial distribution functions given by the scaled particle or Percus-Yevick (PY) theory[4]).

The diameters of the hypothetical hard spheres will be obtained by fitting the experimental pure liquid shear viscosities to the Enskog theory[3]) with scaled-particle or PY contact radial distribution function and solving for the effective hard-sphere diameters σ_1 and σ_2*. The effective hard-sphere

* Present address: Department of Mathematics, California State College at Los Angeles, Los Angeles, California, USA.

** Permanent address: Faculté des Sciences, Université Libre de Bruxelles, Brussels, Belgium.

‡ Present address: Department of Chemistry, State University of New York at Albany, Albany, New York, USA.

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diameter for the interaction of an Ar–Kr pair of molecules, σ_{12}, will be given by the mean value,

$$\sigma_{12} = \tfrac{1}{2}(\sigma_1 + \sigma_2). \tag{1}$$

The predicted shear viscosity of this model is tested on the Ar–Kr mixture experimental results of Boon and Thomaes[6]. The shear viscosity, μ, of the mixture can be represented by this model over the complete composition range with a small *systematic* error. The difference between the calculated value of μ and the observed value of μ is always positive and of the order of 3–5%.

2. *Hard sphere representation of the shear viscosity.* Enskog's formula for the shear viscosity of a fluid of dense hard spheres of diameter σ, number density n, mass m, mass density $\rho = nm$, contact radial distribution function $g(\sigma)$ and $b\rho = \frac{2}{3}\pi n\sigma^3$ is[3])

$$\mu = \mu_{\text{dilute}} \left\{ \frac{1}{g(\sigma)} + \tfrac{4}{5} b\rho + 0.7614\, b^2\rho^2 g(\sigma) \right\} \tag{2}$$

where

$$\mu_{\text{dilute}} = \frac{5}{16\sigma^2} \left(\frac{m k_B T}{\pi} \right)^{\frac{1}{2}}.$$

In the PY theory[4])

$$g(\sigma) = \frac{1 + \dfrac{\pi}{12}\, n\sigma^3}{\left(1 - \dfrac{\pi}{6}\, n\sigma^3\right)^2}. \tag{3}$$

Using eq. (3) in eq. (2) and equating μ to the known experimental values of the shear viscosity of Ar (at 100 K)[7]** and Kr (at 100 K)[7]** one obtains the effective hard sphere diameters shown in table I below:

TABLE I

Effective hard sphere diameters

Inert gas	Effective hard sphere diameter σ	6,12 Lenard-Jones potential	
		diameter σ_{LJ} in Å	energy ε_{LJ}/k_B in K
Argon	3.554×10^{-8} cm	3.465	116
Krypton	4.014×10^{-8} cm	3.61	190

* A hypothetical hard shere fluid model which accounts for the high temperature properties of simple liquids has also been developed by Dymond and Alder[5]).

** The values of the viscosity coefficients at 100 K are obtained from eq. (4) of ref. 7, fitting the experimental data by least squares calculation.

The discrepancy between the listed values for the diameter is larger in the case of Kr. This may be due to the attractive well being deeper for Kr than for Ar.

We shall calculate the shear viscosity of our effective hard sphere mixture employing Thorne's formula[3]) using the diameters listed in table I (column 1) and the experimental molar volume[7]) of the mixture υ_m at mole fraction x_1 of Ar. In this formula subscripts 1 and 2 refer to Ar and Kr respectively, N_A is Avogadro's number, $m_0 = m_1 + m_2$, and g_{11}, g_{22}, and g_{12} are the mixture contact radial distribution functions for Ar–Ar, Kr–Kr and Ar–Kr pairs respectively.

Thus:

$$\mu = \tfrac{5}{2} k_B T \Bigg[b_{-1-1} \left(\frac{x_1}{1 - x_1} \right) \times \left\{ 1 + \frac{4\pi}{15} \frac{N_A x_1}{\upsilon_m} g_{11} \sigma_1^3 + \tfrac{1}{15} \frac{m_2}{m_0} \frac{\pi N_A}{\upsilon_m} (1 - x_1)\, g_{12} (\sigma_1 + \sigma_2)^3 \right\}^2 -$$

$$- 2 b_{1-1} \left\{ 1 + \tfrac{4}{15} \frac{N_A x_1}{\upsilon_m} g_{11} \sigma_1^3 + \tfrac{1}{15} \frac{m_2}{m_0} \frac{\pi N_A (1 - x_1)}{\upsilon_m} g_{12} (\sigma_1 + \sigma_2)^3 \right\} \times$$

$$\times \left\{ 1 + \tfrac{4}{15} \frac{N_A (1 - x_1)}{\upsilon_m} g_{22} \sigma_2^3 + \tfrac{1}{15} \frac{m_1}{m_0} \frac{\pi N_A x_1}{\upsilon_m} g_{12} (\sigma_1 + \sigma_2)^3 \right\} +$$

$$+ b_{11} \left(\frac{1 - x_1}{x_1} \right) \left\{ 1 + \frac{4\pi}{15} \frac{N_A (1 - x_1)}{\upsilon_m} g_{22} \sigma_2^3 + \right.$$

$$\left. + \tfrac{1}{15} \frac{m_1}{m_0} \frac{\pi N_A x_1}{\upsilon_m} g_{12} (\sigma_1 + \sigma_2)^3 \right\}^2 \Bigg] \times$$

$$\times [g_{12}(b_{11} b_{-1-1} - b_{1-1}^2)]^{-1} + \tfrac{4}{15} (\pi k_B T)^{\frac{1}{2}} \left\{ \sqrt{m_1} \left(\frac{N_A x_1}{\upsilon_m} \right)^2 g_{11} \sigma_1^4 + \right.$$

$$\left. + \left(\frac{m_1 m_2}{32 m_0} \right)^{\frac{1}{2}} \frac{N_A^2 x_1 (1 - x_1)}{\upsilon_m^2} g_{12} (\sigma_1 + \sigma_2)^4 + \sqrt{m_2} \frac{N_A^2 (1 - x_1)^2}{\upsilon_m^2} g_{22} \sigma_2^4 \right\}. \tag{4}$$

In eq. (4)

$$b_{11} = b'_{11} + \frac{n_1}{n_2} \frac{g_{11}}{g_{12}} b''_{11},$$

$$b_{-1-1} = b'_{-1-1} + \frac{n_2}{n_1} \frac{g_{22}}{g_{12}} b''_{-1-1},$$

$$b_{1-1} = -\tfrac{8}{3} \left(\frac{\pi m_1 m_2 k_B T}{2 m_0^3} \right)^{\frac{1}{2}} (\sigma_1 + \sigma_2)^2,$$

$$b'_{11} = \tfrac{4}{3}(5m_1 + 3m_2)\left(\frac{\pi m_2 k_B T}{2m_1 m_0^3}\right)^{\frac{1}{2}} (\sigma_1 + \sigma_2)^2,$$

$$b''_{11} = 8\left(\frac{\pi k_B T}{m_1}\right)^{\frac{1}{2}} \sigma_1^2,$$

$$b'_{-1-1} = \tfrac{4}{3}(5m_2 + 3m_1)\left(\frac{\pi m_1 k_B T}{2m_2 m_0^3}\right)^{\frac{1}{2}} (\sigma_1 + \sigma_2)^2,$$

$$b''_{-1-1} = 8\left(\frac{\pi k_B T}{m_2}\right)^{\frac{1}{2}} \sigma_2^2. \tag{5}$$

The scaled particle of PY theory contact radial distribution functions, to be employed in eqs. (4) and (5), are[4])

$$g_{11} = \frac{1 + \dfrac{\pi N_A}{6\upsilon_m}\left\{x_1\left(\dfrac{\sigma_1^3}{2} - \tfrac{3}{2}\sigma_1\sigma_2^2 + \sigma_2^3\right) + \tfrac{3}{2}\sigma_1\sigma_2^2 - \sigma_2^3\right\}}{\left[1 - \dfrac{\pi N_A}{6\upsilon_m}\{x_1(\sigma_1^3 - \sigma_2^3) + \sigma_2^3\}\right]^2}$$

$$g_{22} = \frac{1 + \dfrac{\pi N_A}{6\upsilon_m}\left\{x_1\left(\tfrac{3}{2}\sigma_2\sigma_1^2 - \sigma_1^3 - \dfrac{\sigma_2^3}{2}\right) + \dfrac{\sigma_2^3}{2}\right\}}{\left[1 - \dfrac{\pi N_A}{6\upsilon_m}\{x_1(\sigma_1^3 - \sigma_2^3) + \sigma_2^3\}\right]^2}, \tag{6}$$

$$g_{12} = \frac{\sigma_1 + \sigma_2 + \dfrac{\pi N_A}{3\upsilon_m}\{x_1(\sigma_1^2 - \sigma_2^2) + \sigma_2^2\}\sigma_1\sigma_2 - \dfrac{\pi N_A}{6\upsilon_m}\{x_1(\sigma_1^4 - \sigma_2^4) + \sigma_2^4\}}{(\sigma_1 + \sigma_2)\left[1 - \dfrac{\pi N_A}{6\upsilon_m}\{x_1(\sigma_1^3 - \sigma_2^3) + \sigma_2^3\}\right]^2}.$$

The contact radial distributions were evaluated subject to the assumption (3) using σ_1 and σ_2 from table I and the experimental values of υ_m in eq. (4), subject to eqs. (5) and (6) one obtains the shear viscosity values at 100 K,

TABLE II

Comparison of experimental and computed shear viscosities of Ar–Kr mixtures at 100 K

x_1 = mole fraction of Ar	v_m in cm³	$\mu_{exp.}$ in poise	$\mu_{comp.}$ in poise
0	32.7661	(6.9×10^{-3})	(6.9×10^{-3})
0.2	32.2380	—	5.3606×10^{-3}
0.411	31.6808	3.917×10^{-3}	4.0488×10^{-3}
0.6	31.1818	3.022×10^{-3}	3.1438×10^{-3}
0.8	30.6537	2.274×10^{-3}	2.4014×10^{-3}
1.0	30.1256	(1.81×10^{-3})	(1.81×10^{-3})

shown in the last column of table II. To facilitate comparison we also list the experimental values found by Boon and Thomaes[1,5]). (The values of the experimental and computed shear viscosity coincide for $x_1 = 0, 1$ since these were employed to determine σ_i, $i = 1, 2$.)

The agreement between the last two columns in table II is gratifying; the deviation in all cases being less than 5%, but the deviation is systematic. The computed shear viscosity values are never less than the experimental values for this mixture. This is not astonishing since the molecules of this mixture have a soft intermolecular force contribution and the effective collision diameter of an unlike pair may not satisfy precisely the additivity rule (1).

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