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The Bulk Viscosity in Dense Fluids

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A method for calculating bulk viscosity is described. This method relies on the results of the revised Enskog theory for hard-sphere fluid mixtures and the use of the temperature- and density-dependent diameter of Mansoori–Canfield and Rasaiah–Stell to model each species of the real mixtures. Using this method the predicted values of the bulk viscosity of several mixtures of hydrocarbons and noble gases were calculated. These results are mainly predictive.

KEY WORDS: bulk viscosity; binary mixtures; Enskog theory; kinetic theory.

1. INTRODUCTION

The study of the bulk viscosity (BV) of dense fluids has aroused considerable interest during the past years. However, even though some advances have been made in recent years, our means to obtain theoretical values for the BV of real fluids are still quite limited.

From the experimental standpoint, almost all the experiments carried out to measure BV in real fluids have employed sound attenuation measurements. In these experiments, the BV value is calculated from the excess of the sound absorption actually measured, relative to the classical value, which involves only the shear viscosity and the thermal conductivity. The BV measured in this way are quite uncertain because the absorption excess has different sources, particulary in polyatomic fluids, as we mention later. Presently, experimental BV data are limited to a few fluids, most of them monoatomic and usually involving experimental uncertainties which can be as high as 50% [1, 2]. Examples of these measurements are those of Madigosky on argon [3], Cowan and Ball on argon [4] and krypton [5], Cowan and Leech on xenon [6], and Malbrunot et al. [2] on the same gases near their triple point.

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The bulk viscosity of polyatomic fluids is usually associated with molecular relaxation processes, since the particles of the fluid have, in general, various internal degrees of freedom which can be excited in different ways. The existence of these relaxation processes induces dispersion and absorption of sound waves, thus producing an enhancement of the measured BV. In order to deal with the different contributions to the BV, some authors [1] have explicitly divided them into a part due to molecular and collisional contributions and another due to the internal degrees of freedom. In particular, we are interested in developing predictive methods for the former, i.e., for the intrinsic BV of simple fluids and their mixtures.

Another approach to estimate the BV values of fluids is based on molecular dynamics simulations of systems modeled by the Lennard-Jones potential. Starting with the work of Levesque et al. [7], all simulations have been limited to the vicinity of the triple point [8–10].

Kinetic theory gives a third alternative to obtain the BV of fluids modeled by simple interatomic potentials. Earlier work on dilute monoatomic fluids using the Boltzmann equation showed that they do not have BV [11]. This was not the case for dilute polyatomic fluids [12, 13]. In order to obtain transport coefficients in dense fluids, Enskog generalized the Boltzmann equation to describe the hard-sphere dynamics in the dense regime [11]. This theory was later extended in order to deal with binary [11] and multicomponent [14] dense hard-sphere fluid mixtures, but the extensions were found to be inconsistent with irreversible thermodynamics [15]. The inconsistency was resolved by van Beijeren and Ernst [16], who proposed what is called the revised Enskog theory (RET). Explicit expressions for the BV of mixtures were derived and discussed in detail by Karkheck and Stell [17] and Lopez de Haro et al. [18], whose formulas are the basis for our predictive method. Another related work was done by Hanley and Cohen [1] in the framework of the modified Enskog eqation (MET), but it has not been able to extend this approach to mixtures.

The main difficulty in applying the RET bulk viscosity formulas to real fluids lies in relating the contact values of the hard-sphere radial distribution function and the hard-sphere diameters appearing in the theory to quantities associated with real systems. Our procedure to achieve this connection is presented in Section 2. In Section 3, the results of our calculations are presented for several one-component and binary mixtures.

2. THE BULK VISCOSITY OF DENSE FLUIDS

Our starting point is the set of coupled nonlinear kinetic equations for multicomponent hard-sphere mixtures in the RET first given by van Beijeren and Ernst [16]. In the case of a binary mixture and in the absence of an outside field, this set consists of two coupled nonlinear integrodifferential equations for the two-single-particle distribution function $f_i(\vec{r}, \vec{v}_i, t)$ $(i = 1, 2)$:

$$\left[\frac{\partial}{\partial t} + \vec{v} \cdot \frac{\partial}{\partial \vec{r}}\right] f_i(\vec{r}, \vec{v}_i, t) = \sum_{j=1}^{2} J_{ij}(f_i f_j) \tag{1}$$

where

$$\begin{aligned} J_{ij}(f_i f_j) = \iint & (\hat{k} \cdot \vec{v}_{ji}) \theta(\hat{k} \cdot \vec{v}_{ji}) \sigma_{ij} [\chi_{ij}(\vec{r}, \vec{r} + \sigma_{ij}\hat{k} \mid \{n_k\}) f_i(\vec{r}, \vec{v}_i', t) \\ & \times f_i(\vec{r} + \sigma_{ij}\hat{k}, \vec{v}_i', t) - \chi_{ij}(\vec{r}, \vec{r} - \sigma_{ij}\hat{k} \mid \{n_k\}) \\ & \times f_i(\vec{r}, \vec{v}_i, t) f_i(\vec{r} - \sigma_{ij}\hat{k}, \vec{v}_i, t)] \, d\hat{k} \, d\vec{v}_j \end{aligned}$$

Here $f_i(\vec{r}, \vec{v}_i, t)$ is the average number of hard spheres of component i (with diameter σ_i and mass m_i) at the position $\vec{r}$ with velocity $\vec{v}_i$ at time t; $\vec{v}_{ji} = \vec{v}_j - \vec{v}_i$ is the relative velocity of two spheres with velocities $\vec{v}_i$ and $\vec{v}_j$, respectively; $\hat{k}$ is a unit vector directed along the line of centers from the sphere of component j to the sphere of component i upon collision (i.e., at contact); and θ is the Heaviside step function. $\vec{v}_i'$ and $\vec{v}_j'$ denote the velocities of the restituting collision, which are connected to those of the direct collision $\vec{v}_i$ and $\vec{v}_j$ by the relations

$$\begin{aligned} \vec{v}_i' &= \vec{v}_i + 2M_{ji}(\hat{k} \cdot \vec{v}_{ji})\hat{k} \\ \vec{v}_j' &= \vec{v}_j - 2M_{ij}(\hat{k} \cdot \vec{v}_{ij})\hat{k} \end{aligned}$$

where $M_{ij} = m_i/(m_i + m_j)$. χ_{ij} is the radial distribution function of two hard spheres, one of component i and the other of component j, at contact, i.e., when the distance between their centers is $\sigma_{ij} = (\sigma_i + \sigma_j)$. In the RET, the χ_{ij}'s are the same functional of the local number densities $\{n_i\}$ as in a binary mixture in nonuniform equilibrium. The molecular fluxes and the transport coefficients for dense hard-sphere binary mixtures, up to the Navier-Stokes level, can be directly obtained from Eqs. (1) on the basis of the procedure used in Ref. 18, and we do not repeat the derivation here. Instead we quote only the relevant results. It turns out that the momentum flux $\overleftrightarrow{P}$ is given by

$$\overleftrightarrow{P} = p\overleftrightarrow{I} - 2\eta \overset{\circ}{\overline{\overline{\frac{\partial u}{\partial \vec{r}}}}} - \kappa \left(\frac{\partial}{\partial \vec{r}} \cdot \vec{U}\right) \overleftrightarrow{I}$$

where

$$p = \sum_{i=1}^{2} n_i k_B T \left(1 + \sum_{j=1}^{2} \rho b_{ij} \chi_{ijc}^{HS}\right) \tag{2}$$

is the thermostatic pressure, $\vec{I}$ is the unit tensor, η is the coefficient of shear viscosity, κ is the bulk viscosity, $\vec{U}$ is the hydrodynamic velocity, and the symbol $\triangleq$ denotes the symmetric traceless part. In Eq. (2), $\rho b_{ij} = 2\pi n_j \sigma_{ij}^3/3$, k_B is Boltzmann's constant, T is the absolute temperature, and χ_{ijc}^{HS} is the equilibrium value of the radial distribution function for spheres of species i and j at contact, where the equilibrium density has been replaced by the local equilibrium density $n = n_1 + n_2$. Explicit expressions for η and κ for binary mixtures in terms of the molecular parameters are given in Refs. 18 and 22. The latter reads

$$\kappa = \frac{4}{9} \sum_{i=1}^{2} \sum_{j=1}^{2} \left(\frac{2\pi m_i m_j k_B T}{m_i + m_j} \right)^{1/2} n_i n_j \sigma_{ij}^4 \chi_{ijc}^{HS}$$

$$+ 2k_B T \sum_{i=1}^{2} \frac{n_i}{n} \left(\sum_{j=1}^{2} \rho b_{ij} M_{ji} \chi_{ijc}^{HS} \right) h_1^{(i)} \tag{3}$$

where the $h_1^{(i)}$ are coefficients that appear in the Sonine polynomial expansion of the one-particle distribution functions. In the so-called Nth Enskog approximation, i.e., when N Sonine polynomials are taken into account in the expansion, the $h_1^{(i)}$ are determined from a set of linear equations (for details see Ref. 18).

The evaluation of κ for given $\{n_i\}$, $\{\sigma_i\}$, $\{m_i\}$, and T using Eq. (3) requires knowledge of χ_{ijc}^{HS}. An exact, explicit equation for χ_{ijc}^{HS} in terms of the number densities and the set of hard-sphere diameters is not available, but several approximate expressions already exist. In particular, the so-called Carnahan–Starling [19] approximation appears to be quite accurate when compared to molecular dynamics data.

In order to use Eq. (3) to obtain numerical estimates of the BV of real mixtures, we need a prescription to get state-dependent hard-sphere diameters in terms of the parameters associated with the potentials chosen to model the actual systems. While several routes are possible, we follow the one taken in our previous work [20–22], namely, we consider that each component of the binary mixture is modeled through a Lennard-Jones potential

$$\Phi_i^{LJ}(r) = 4\varepsilon_i \left[\left(\frac{\sigma_{0i}}{r} \right)^{12} - \left(\frac{\sigma_{0i}}{r} \right)^{6} \right]$$

where ε_i is the well depth and σ_{0i} is the minimal separation of two molecules of species i such that $\Phi_i^{LJ}(\sigma_{0i}) = 0$, and we determine separately the effective diameters in terms of σ_{0i}, ε_i, and the thermodynamic state of the system. As for the cross interaction, we assume it to be that of a hard-sphere mixture with effective diameters, i.e.,

$$\sigma_{12} = \sigma_{21} = (\sigma_1 + \sigma_2)/2$$

The effective diameters $\sigma_i (i = 1, 2)$, can be obtained by several schemes well stablished in equilibrium liquid state theory. Our previous work showed us that the variational method of Mansoori–Canfield and Rasaiah–Stell (MC/RS) is the best suited for our task [20–22].

3. NUMERICAL RESULTS AND DISCUSSION

Values for the BV of several monocomponents and binary systems were calculated following the method described above, i.e., the bulk viscosities were obtained from Eq. (3) up to the 10th Enskog approximation with the effective state-dependent diameters calculated with

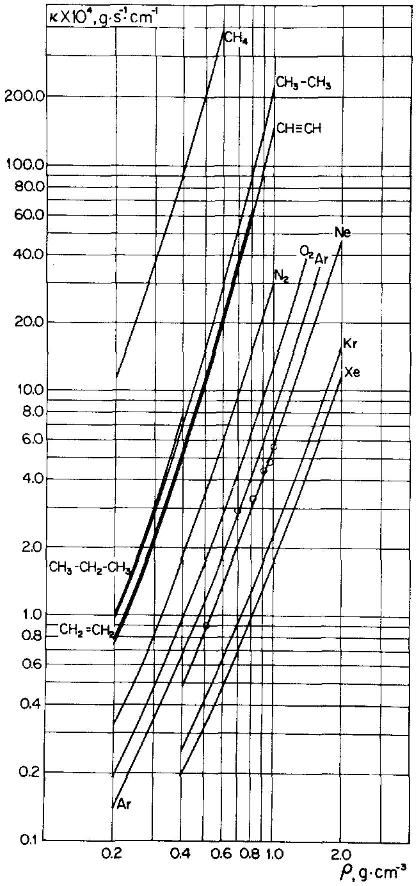

Fig. 1. The calculated values of the bulk viscosity versus the mass density for 11 monocomponent systems at 234.5 K (○) Experimental data for argon [3].

the MC/RS prescription and the χ_{ijc}^{HS} evaluated with the Carnahan–Starling approximation.

Figure 1 shows the calculated values of the BV versus the mass density for 11 monocomponent systems in a log–log plot, at 234.5 K. For argon we plotted the experimental data of Madigosky [3], and for the other fluids our calculations are predictive since there is no experimental measurements. As we can see from Fig. 1, there is a rough linear relation between log κ and log ρ, consistent with the approximate relation $\kappa \sim \rho^2$.

Figure 2 shows in a semilog plot the calculated values of the bulk viscosity for several binary mixtures of neon at 300 K at a very high density (molar density fixed to 0.03 mol/cm^3 in all calculations). All calculations are predictive.

Figure 3 shows the ratio of bulk to shear viscosities versus the reduced density ($n^* = n\sigma^3$) for three noble gases and several binary systems. The shear viscosity was calculated with the same formalism as that presented in

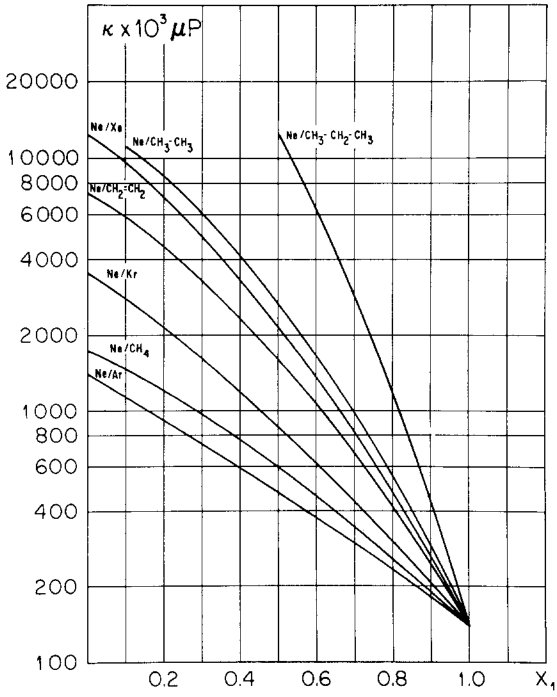

Fig. 2. The calculated values of the bulk viscosity for several binary mixtures of neon at 300 K at a very high density (0.03 mol · cm^{-3} in all calculations) versus the mole fraction.

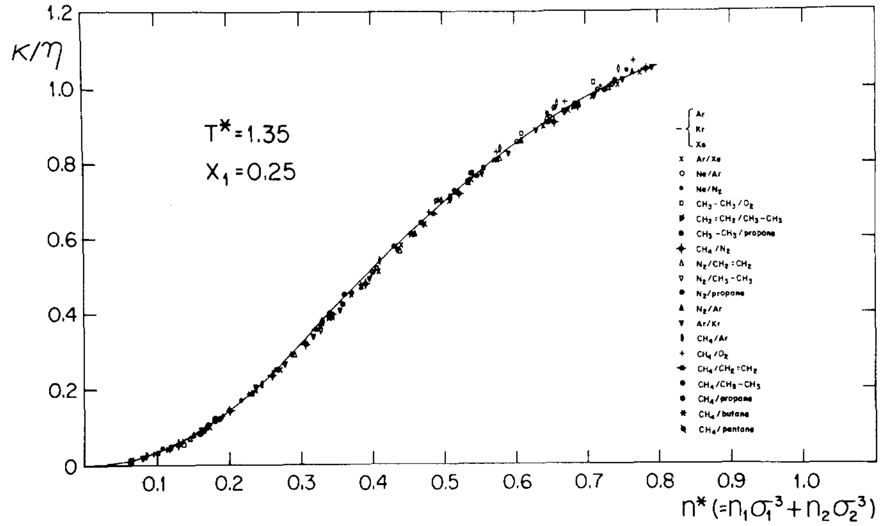

Fig. 3. The ratio of bulk to shear viscosities versus the reduced density of a few monocomponent and several binary systems ($X_1 = 0.25$) at $T^*(=kT/\varepsilon) = 1.35$.

Section 2 (see Refs. 22–24). We can see two interesting features: (a) at high densities the intrinsic bulk viscosity is a physical property as important in magnitude as the shear viscosity; and (b) all systems relate the ratio of bulk to shear viscosities to the reduced density in the same form as if a corresponding state principle were obeyed. Although this quantity κ/η can follow a corresponding state law as suggested by Cowan and Leech [6] from experimental determinations, in our case this correspondence is built-in by the hard-sphere approach and in some way it is a proof of the internal consistency of the method.

At lower temperatures Fig. 3 changes slightly to higher values, but there were no changes for calculations made at different concentrations. In particular, for concentrations of $X_1 = 0.5$ and $X_1 = 0.75$ (not shown in Fig. 3), we obtain the same curve as in Fig. 3. One interesting application of the curve defined in Fig. 3 could be to use it in conjunction with some realistic method to predict the shear viscosity of hydrocarbons [as the TRAPP procedure given by Ely and Hanley (23, 24)] in order to obtain good estimates of bulk viscosities of these compounds. This study is under way and will be described in a coming paper.

In summary, these results are encouraging and could be a point of departure to obtain multicomponent bulk viscosities. However, the lack of experimental and molecular dynamics results is a hindrance to testing our method.

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