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The Molecular Roughness Factor from the Bulk Viscosity Coefficient

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The translational–rotational coupling factor, or roughness factor, introduced by Chandler, has been evaluated for two types of nonpolar liquids along the saturation line. For the first type (atomic liquids), a universal correlation has been found. For the second type (alkanes), this quantity presents a sharp increase in the neighborhood of the solid–fluid transition for hard spheres. This parameter plays an essential role, since it allows a link to be established between simulation and experimental data.

KEY WORDS: bulk viscosity; roughness factor; saturation line.

1. INTRODUCTION

The usual hard-sphere model or smooth hard-sphere model (SHS) is a fruitful tool for the description of atomic liquids if the hard-sphere diameter σ depends on the state variables (temperature and pressure). For extending the description to molecular liquids, Chandler [1] introduced the rough hard-sphere model (RHS) as a system composed of spherical particles which collide impulsively. These instantaneous collisions are capable of changing the angular momentum of a particle as well as the linear momentum. Chandler's description requires a new parameter: the translational–rotational coupling factor or roughness factor A_X, where X is a transport property. Chandler assumed that the X coincides with the corresponding value for the rough hard-sphere model X_{RHS}, which can be related to the value for the smooth hard-sphere model X_{SHS} by

$$X = X_{\mathrm{RHS}} = A_X X_{\mathrm{SHS}}(\sigma) \qquad (1)$$

The hard-sphere diameter, σ, is easily related to the close-packed volume V_0 and the number N of particles by means of $V_0 = N\sigma^3/2^{1/2}$.

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In this paper the analyzed transport property X is the bulk viscosity coefficient κ. In earlier works [2–5], we calculated the roughness factor for other transport properties: the self-diffusion, shear viscosity, and thermal conductivity coefficients. The results were highly encouraging: each substance is well represented by a unique value of A_X and this quantity tends to unity for atomic liquids. Given that this quantity is the expected value for these substances, the results obtained justify the method employed. However, in the case of the bulk viscosity coefficient, these results change substantially. Therefore the original meaning for this quantity is lost. Nevertheless, new and interesting results appear subsequently.

The method has been described in Refs. 2–4 and here we quote only the results required for our later development.

We start with the expression

$$\kappa = \kappa_{\mathrm{RHS}} = A_\kappa \kappa_{\mathrm{E}}(\kappa_{\mathrm{SHS}}/\kappa_{\mathrm{E}}) \tag{2}$$

The Enskog value κ_{E} is related to the shear viscosity coefficient η_0 of a dilute gas composed of hard spheres by means of

$$\kappa_{\mathrm{E}} = \eta_0 1.002\ g(\sigma)(b/V) \tag{3}$$

with

$$\eta_0 = (\tfrac{5}{16}\sigma^2)(mk_{\mathrm{B}}T/\pi)^{1/2} \tag{4}$$

where m is the molecular mass, k_{B} is Boltzmann's constant, and T is the temperature. The radial distribution function $g(\sigma)$ and the covolume b/V are expressed as

$$Z = 1 + (2\pi\sigma^3/3)\, ng(\sigma); \qquad b/V = (2\pi/3)\, n\sigma^3 \tag{5}$$

where Z is the compressibility factor, n the number density, and V the molar volume.

Denoting molar mass M and substituting in Eq. (3), we obtain

$$\kappa_{\mathrm{E}} = C(MT)^{1/2}(V_0/V)(Z-1)/\sigma^2 \tag{6}$$

where C is a substance-independent constant.

The value of κ_{E} is now immediate because M, T, and V are introduced directly, and σ can be obtained from an appropriate expression relating the variation of the hard-sphere diameter to temperature and pressure, although the latter has only a minor influence. Finally, Z can be obtained from a fit of the available simulation data by means of a polynomial formula in the stable and metastable ranges [6–8].

The experimental values for the bulk viscosity coefficient κ are obtained from the following expression [9]:

$$\kappa = \frac{\alpha \rho c^3}{2\pi^2 f^2} - \left(\frac{\gamma - 1}{C_P} \lambda + \frac{4}{3} \eta_s \right) \tag{7}$$

where α/f^2, ρ, c, γ, C_P, λ, and η_s represent, respectively, the ultrasonic absorption, the density, the sound velocity, the ratio between specific heat capacities C_p and C_V, the specific heat capacity at constant pressure, the thermal conductivity coefficient, and the shear viscosity coefficient. This equation introduces the bulk viscosity from the measured sound absorption by subtracting the calculated value of the classical absorption, given by the last two terms in Eq. (7).

The existing experimental measurements for α/f^2 determine the values available for κ, which are generally scarce. On the other hand, κ_{SHS}/κ_E is provided by the simulation data. Again, the scarcity of available information is significant. This is true for all transport properties, but it is particularly important in the case of the bulk viscosity coefficient. In fact, to our knowledge, simulation data for κ_{SHS}/κ_E as a function of V_0/V are available only from Alder et al. (AGW) [10] and Joslin et al. (JGMK) (taken from their limit of a square-well fluid) [11]. We have fitted κ_{SHS}/κ_E as a function of V_0/V by means of a polynomial whose degree is the highest possible permitted by the data in the above-mentioned references. The result for the two simulations (AGW and JGMK) is

$$\begin{aligned} \kappa_{SHS}/\kappa_E = {} & 9.69 \times 10^{-1} - 1.02 \times 10 (V_0/V) + 3.69 \times 10^2 (V_0/V)^2 \\ & - 3.81 \times 10^3 (V_0/V)^3 + 1.73 \times 10^4 (V_0/V)^4 - 3.88 \times 10^4 (V_0/V)^5 \\ & + 4.27 \times 10^4 (V_0/V)^6 - 1.83 \times 10^4 (V_0/V)^7 \end{aligned} \tag{8}$$

$$\kappa_{SHS}/\kappa_E = -0.568 + 14.9 (V_0/V) - 45.2 (V_0/V)^2 + 42.5 (V_0/V)^3 \tag{9}$$

Finally, Eq. (2) gives the value of A_κ.

2. RESULTS AND DISCUSSION

We have classified the liquids into two groups: (a) apolar atomic liquids (Ne, Ar, Kr, and Xe) and (b) n-alkanes or normal paraffins (C_nH_{2n+2}, with $n = 1$–10, 12, 14).

The hard-sphere diameter for atomic liquids was taken from the expression proposed by Nezbeda and Aim [12]:

$$\ln \frac{\sigma}{d_a} = -0.03125 \ln \frac{T}{T_t} - 0.00540 \ln^2 \frac{T}{T_t} \tag{10}$$

where T_t is the triple-point temperature and $d_a = 0.2880, 0.3461, 0.3703$, and 0.4004 nm for Ne, Ar, Kr, and Xe, respectively.

The only results available for Ne, to our knowledge, are those reported by Larsen et al. [13], who measured the ultrasonic velocity c and attenuation α/f^2 between 25 and 37 K. Fortunately, the situation for the other three liquids is much better. Experimental measurements have been made by several groups of researchers for Ar [14–22], Kr [14, 15, 19, 20, 23, 24], and Xe [14, 15, 19, 20, 24, 25].

Figure 1 shows the results of κ for Ne and for Ar, Kr, and Xe, published by authors who have measured the bulk viscosity for the three substances [14, 19–21, 23, 25]. The neon data are clearly different from the rest and cannot be compared with other estimations. Consequently, we have not attempted to draw conclusions from them. A possible explanation for this behavior is the following. Frequently the neon properties differ appreciably with respect to the rest. This is attributed usually to the existence of quantum effects, although this justification cannot be completely satisfactory. Moreover, in our case, the neon data are unique. Therefore possible experimental errors cannot be detected. For the remaining substances, a wide dispersion, which advises a separate analysis for each reference, is observed.

We have evaluated A_κ combining each experimental estimation for Ar, Kr, and Xe, shown in Fig. 1, with the two simulations [10, 11] cited

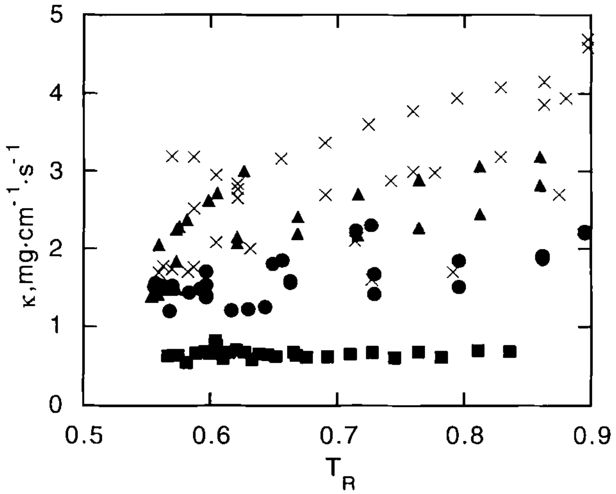

Fig. 1. Plot of the bulk viscosity coefficient κ as a function of reduced temperature $T_R = T/T_C$ for apolar atomic liquids: neon (■), argon (●), krypton (▲), and xenon (X).

above. The best results for A_κ are obtained by taking the experimental data of Mikhailenko et al. [14] together with the simulation data of Joslin et al. [11].

Plotting A_κ against the reduced temperature $T_R = T/T_C$, the points corresponding to Ar, Kr, and Xe lie approximately on the same curve (Fig. 2), thus satisfying the law of corresponding states. Whereas T_R is the preferred independent variable from an experimental point of view, V_0/V is the natural independent variable from a simulation study. Moreover, T_R and V_0/V are easily related [3]. Therefore we have plotted A_κ against V_0/V (Fig. 3) obtaining the same conclusion. Finally, from the statistical mechanics viewpoint, the most adequate independent variable is the reduced temperature $T^* = k_B T/\varepsilon$, where the constant ε of the Lennard-Jones potential was taken from Bewilogua and Gladun [26]. The corresponding plot (Fig. 4) also shows a good correlation. The Ar, Kr, and Xe data have not been separated in these figures in order to emphasize the common behavior.

For numerical applications, we give the coefficients of the fitting function:

$$A_\kappa = 359.81 - 2040.4T_R + 4307.6T_R^2 - 4015.0T_R^3 + 1399.7T_R^4 \qquad (11)$$

with a correlation coefficient $r = 0.99609$.

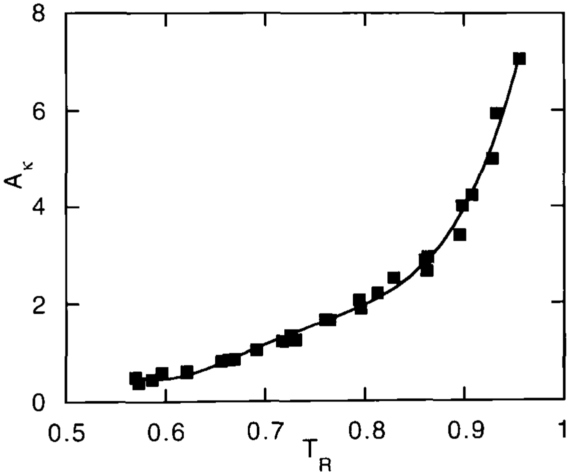

Fig. 2. Plot of the roughness factor A_κ as a function of reduced temperature T_R for argon, krypton, and xenon: experimental points (■); fitting line (—).

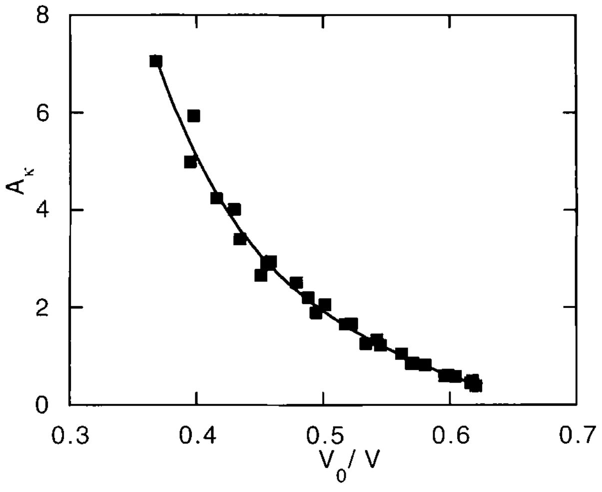

Fig. 3. A_K as a function of V_0/V for argon, krypton, and xenon: experimental points (■); fitting line ( ).

An experimental result, valid also for isolated measurements of other simple liquids such as oxygen, nitrogen, and methane, is the increase in ultrasonic absorption with temperature, which implies a correlative increase in the bulk viscosity coefficient and the roughness factor, in accordance with our results.

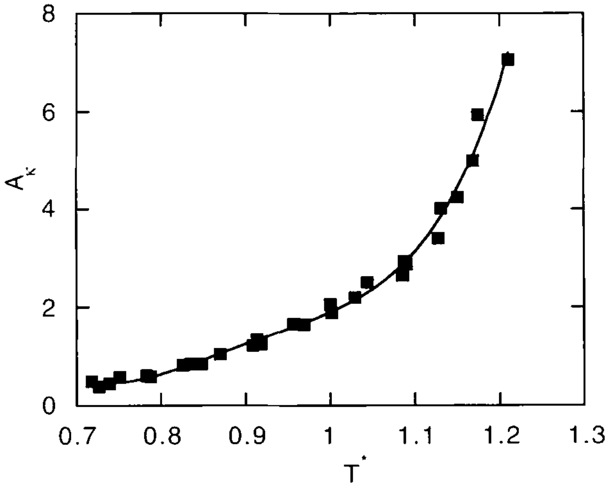

Fig. 4. A_K as a function of $T^* = k_B T/\varepsilon$ for argon, krypton, and xenon: experimental points (■); fitting line (—).

For alkanes, the hard-sphere diameter was obtained from the correlation proposed by Assael et al. [27] for V_0 as a function of carbon number C and temperature T with the following results.

CH_4-C_4H_{10}:

$$\begin{aligned}10^6 V_0 = {} & 45.822 - 6.1867T^{0.5} + 0.36879T - 0.007273T^{1.5} \\ & + C(2.17871T^{0.5} - 0.185198T + 0.00400369T^{1.5}) \\ & + C^2(6.95148 - 52.6436T^{-0.5}) \\ & + C^3(-7.801897 + 42.24493T^{-0.5} \\ & + 0.4476523T^{0.5} - 0.009573512T)\end{aligned} \tag{12}$$

C_5H_{12}-$C_{16}H_{34}$:

$$\begin{aligned}10^6 V_0 = {} & 117.874 + 0.15(-1)^C - 0.25275T + 0.000548T^2 \\ & - 0.0000004246T^3 + (C-6)(1.27 - 0.0009T)(13.27 + 0.025C)\end{aligned} \tag{13}$$

Here the information for obtaining A_κ is less satisfactory. In fact, Singer [28] measured the ultrasonic attenuation in liquid methane but only three points are close to the saturation line. Piercy and Rao [29] and Cochran et al. [30] have provided a considerable amount of experimental data for the higher alkanes. Since the two sets of measurements are hardly compatible, we have used the data in Ref. 29, which covers a wider range.

In contrast to the simple liquids, the ultrasonic absorption of alkanes (except for methane) decreases with temperature and increases with V_0/V. This behavior can be extended to the bulk viscosity coefficient and the roughness factor.

Figure 5 shows A_κ versus V_0/V for the alkanes. A similar but opposite trend is obtained by replacing V_0/V with T_R (Fig. 6). Except for propane, a decrease with the mass of the alkane is observed. Although the entire possible range is not plotted for alkanes and the dispersion among them is larger than for the simple liquids, the range for V_0/V (and T_R) is wider in this case. This furnishes additional results. Thus, the existence of three regions is clearly evident. In the first region ($V_0/V < \approx 0.58$), A_κ increases smoothly; and in the second region ($0.58 < V_0/V < 0.67$), A_κ is approximately constant, but in the third region ($V_0/V > \approx 0.67$), A_κ increases sharply. The latter behavior is also observed for the shear viscosity coefficient [3], and its lower limit practically coincides with the value of V_0/V corresponding to a solid–fluid transition for a hard-sphere system. In

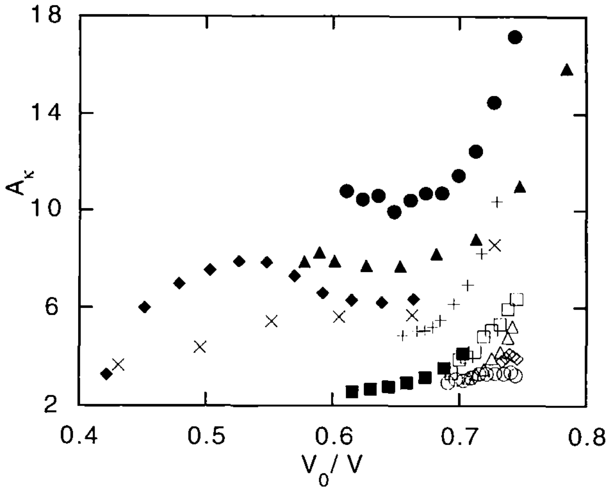

Fig. 5. A_κ as a function of V_0/V for the alkanes: propane (■); butane (●); pentane (▲); hexane (◆); heptane (X); octane (+); nonane (□); decane (○); dodecane (△), and tetradecane (◇).

Table I, we give analytical expressions for the variation of A_κ for the entire available range (nonane, decane, dodecane, and tetradecane have been excluded because the range is too small) of the form

$$A_\kappa = a + b(V_0/V) + c(V_0/V)^2 + d(V_0/V)^3 + e(V_0/V)^4 \qquad (14)$$

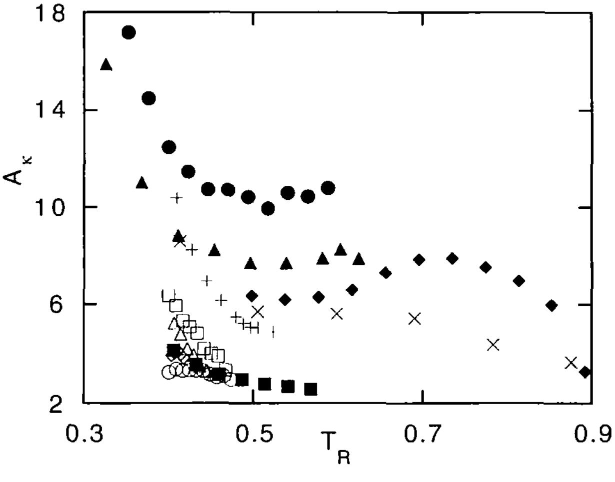

Fig. 6. A_κ as a function of T_R for the alkanes. Symbols the same as in Fig. 5.

Table I. Values of the Parameters *a*, *b*, *c*, *d*, *e*, and the Correlation Coefficient

Alkane	Po	Range of V_0/V	$a \times 10^{-2}$	$b \times 10^{-2}$	$c \times 10^{-3}$	$d \times 10^{-3}$	$e \times 10^{-3}$	r
Propane	7	0.616–0.703	8.641	−59.92	15.52	−17.76	7.594	0.99992
Butane	11	0.610–0.743	36.36	−230.0	55.03	−58.80	23.66	0.99683
Pentane	9	0.578–0.784	7.086	−47.45	12.08	−136.8	5.816	0.99863
Hexane	11	0.422–0.663	−0.782	−0.802	2.023	−4.448	2.820	0.99389
Heptane	6	0.431–0.727	6.547	−48.49	13.55	−16.12	7.214	0.99990
Octane	9	0.655–0.729	435.5	−2567	567.9	−559.0	2066	0.99960

Heptane is perhaps the only substance with the three regions here present. Also, its correlation is very good with respect to the other alkanes. This fact hints that the behavior would be the same for the remaining ones if the whole range were available.

3. CONCLUSIONS

A simple method for characterizing the behavior of the roughness factor A_κ of several liquids on the saturation line has been developed. With this method, for a given temperature, we require experimental data (almost all the thermophysical properties, equilibrium, and transport), the hard-sphere diameter, the ultrasonic absorption, and simulation results for the bulk viscosity coefficient. The requirement for such a high number of parameters restricts the amount of results obtained. For apolar atomic liquids, a correlation with T_R (or V_0/V) is observed. For alkanes, for which fewer data are available, a common relation seems problematic. However, the increase in the range for V_0/V reveals a sharp variation in A_κ for the density corresponding to the solid–fluid transition for hard spheres. This agrees with the expected behavior for the viscosity in the transition toward more ordered states and the considerable strenghthening of the attractive forces.

From a practical point of view, A_κ links simulation and experimental data for the bulk viscosity coefficient, thus allowing their mutual interconversion. This feature is the key motivation for performing this study.

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