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Effective Sizes of Spherical and Linear Molecules

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Abstract. The effective sizes of Ar, CH_4 and CO_2 are obtained by a method based on corresponding states. The effective sizes are in agreement with calculations of the effective diameters based on perturbation theories. It is shown that the ratio of the diameters of Ar and CH_4 is constant, reflecting the fact that these molecules are approximately conformal. The behaviour of the effective diameter of CO_2 shows the effect of the shape of this molecule.

Resumen. En este trabajo se presentan tamaños efectivos de Ar, CH_4 y CO_2 obtenidos a partir de un método basado en estados correspondientes. Estos tamaños concuerdan con los diámetros efectivos que se calculan mediante teorías de perturbaciones. Se muestra aquí que la razón entre los diámetros de Ar y CH_4 es constante, lo cual refleja el hecho de que estas moléculas son aproximadamente conformes. El comportamiento de los diámetros efectivos del CO_2 muestra el efecto de la forma de esta molécula.

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1. Introduction

Recently, a method to obtain effective sizes of soft non-spherical repulsive particles has been proposed [1]. This method allows to calculate an equivalent hard-sphere (HS) diameter from thermodynamic data which can be related to the diameters used in the Barker-Henderson (BH) and Weeks-Chandler-Andersen (WCA) perturbation theories [2,3]. The method was referred to as Method of Corresponding Systems (MCS) and consist of a modification of the Generalized Principle of Corresponding States [4] (GPCS). A possibility of extending the MCS to real substances has been proposed [5]. In this work we present the effective diameters of three real substances (Ar, CH_4 and CO_2) on orthobaric liquid states, obtained with the MCS.

The effective diameters obtained from the above methods depend in general on density and temperature $\sigma = \sigma(\rho, T)$. The temperature dependence of σ arises from the softness of the repulsive interactions (σ is independent of T for hard particle systems) and its density dependence is due to the softness and the eccentricity of the particles. In particular, the functions $\sigma(\rho, T)$ of two conformal systems differ only by a scale factor, in agreement with the GPCS, but for elongated particles, as hard-dumbells and spherocylinders, σ decreases with density more strongly than for spherical ones. The analysis of the effective diameters of Ar, CH_4 and CO_2 should allow the test of these predictions.

2. Effective Diameters from the MCS

In order to obtain the effective parameters of a given substance S at a state of density ρ and temperature T, the MCS uses a model reference substance S_0 at the same state (ρ, T) and chooses the parameters of S_0 so that the pressures P and P_0 of S and S_0 become equal. For purely repulsive systems, the reference S_0 is simply the fluid of HS with diameter σ [1] and the equality $P = P_0$ is enough to obtain $\sigma(\rho, T)$. Nevertheless, for real substances one needs a reference S_0 which has an attractive force besides the HS repulsion. This has been done with a square-well (SW) systems whose parameters are: σ, the hard-core diameter; ϵ, the depth of the well, and R, the range of the attractive force. In this same case of real fluids one needs two more relations, besides $P = P_0$, to obtain the parameters.

The SW equation of state used was the well known 2nd-order approximation of BH. This written as

$$Asw/NkT = a_{\mathrm{HS}}(\rho^*) + \frac{\epsilon}{kT} a_1(\rho^*, \lambda) + \left(\frac{\epsilon}{kT}\right)^2 a_2(\rho^*, \lambda), \qquad (1)$$

where a_{HS} is the Helmholtz free energy of a HS system; $\rho^* = \rho\sigma^3$ and $\lambda = R/\sigma$. Henderson, Scalise and Smith (HSS) [6] calculated the values of a_1 and a_2 for a set of values of λ between 1.125 and 2, by means of Monte Carlo simulations and gave an explicit expression that fits $a_1(\rho^*)$ and $a_2(\rho^*)$ at each value of λ. This expression is

$$a_i(\rho^*) = C_i\left\{1 - \exp[\alpha_i\rho^*/(\beta_i - \rho^*)] - \alpha_i\rho^*/\beta_i\right\} + P_i\rho^* + Q_i\rho^{*2}, \tag{2}$$

where $i = 1, 2$. The values of the coefficients α_i, β_i, C_i, P_i, Q_i, were communicated by HSS and with them Eq. (2) reproduces the MC data within its uncertainty. The orthobaric thermodynamic properties of the SW fluid were calculated for each λ from these equations [7].

In this application the depth ϵ was chosen constant, as in the perturbation theory with the same reference [8]. For each orthobaric state of S, at temperature T and with density ρ and pressure P_σ, we chose σ and R such that S_0 at the same (ρ_σ, T), is also at an orthobaric state and with P_0 equal to P_σ. These two conditions lead to the following equations:

$$P_\sigma = \frac{\epsilon}{\sigma^3} P_\sigma^*(T^*, \lambda) \tag{3}$$

and

$$P_\sigma(T) = \frac{1}{\sigma^3} P_\sigma^*(T^*, \lambda), \tag{4}$$

where $P^* = P_0\sigma^3/\epsilon$ and $T^* = kT/\epsilon$. These equations have to be solved for σ and λ (or R) at each state. The LHS of Eqs. (3) and (4) is obtained from experimental values for the systems S.

The values of ϵ were chosen in such a way that Eqs. (3) and (4) have a solution for the saturated vapour as close to the critical point as possible, which occurs for $T^* = 1.2$ where the critical compressibility factor of S_0 takes its minimum value $Z_c^\circ = 0.372$. The factor that this value is higher than Z_c for real simple fluids prevents the selection of ϵ at the critical point itself and is due to the approximate nature of the 2nd order expression for the equation of state of S_0. Furthermore, the effective parameters σ and R (or λ) obtained for real substances were proven to be independent of the precise value of ϵ, except for a scale factor close to one.

3. Results

The depths of the potential wells of Ar, CH_4 and CO_2 were found to be 125.2 K, 158.3 K, respectively. The orthobaric properties of Ar, CH_4 and CO_2 used in the MCS were those given in Refs. 9–11. The effective diameters of the argon molecule at orthobaric vapour and liquid states are shown in Fig. 1. At each temperature, $\sigma_V > \sigma_L$ in agreement with the perturbation theory prediction that σ decreases with ρ. To obtain $\sigma(T)$ at constant ρ, a truncated two-term virial expansion of $\sigma(\rho, T)$, of the form $\sigma = \sigma_0(T) + \sigma_1(T)\rho$, was used at each T. Figure 1 shows an example of $\sigma(T)$ at constant ρ, which also agrees with the statistical mechanics in that σ decreases with T. These isochoric diameters $\sigma(T)$ can be compared in Fig. 1 with the density independent diameters found by Aim and Nezbeda [12].

Nevertheless, the values of σ_V shown in the same figure do not decrease monotonically along the orthobaric states, which disagrees with theoretical predictions. Since statistically σ is a mean collision diameter, it should be smaller than the distance r_m to the minimum of the intermolecular potential $u(r)$, and close to r_0, the distance where $u(r_0) = 0$. For argon, the very accurate potential of Azis and Chen [13], gives $r_m = 3.759$ Å (1Å $= 0.1$ mm) and $r_0 = 3.35$ Å. From Fig. 1, it is clearly seen that, for the saturated liquid, $r_m > \sigma_L \cong r_0$ as it should. Nevertheless, for the saturated vapour it was found that $\sigma_V > r_m$, which indicated an error in the values of σ_V. The effective diameters of the Ar, CH_4 and CO_2 molecules at orthobaric liquid states are shown in Fig. 2. The increase of σ with T observed in all cases is due to the combined effect of increasing T and decreasing ρ along the saturated liquid line. It is apparent from the same figure that $\sigma_L(\text{Ar})$ and $\sigma_L(CH_4)$ have the same behaviour

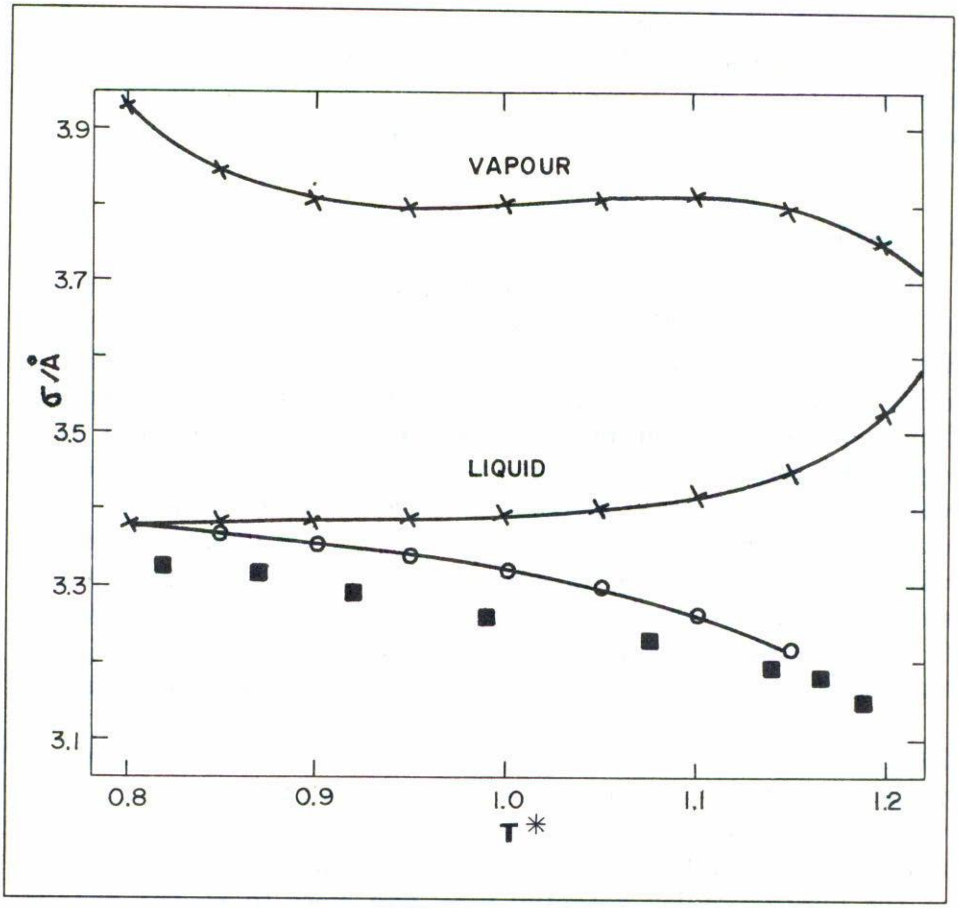

FIGURE 1. Effective diameters for argon obtained by the; MCS. (×), orthobaric states; ○, isochoric liquid states for $\rho^* = 0.033$, ■, BH diameters obtained by Aim and Nezbeda. The lines through the points are graphical interpolations.

with T and ρ, which agrees with the fact that the two molecules are approximately conformal, in agreement with independent CS information. Indeed one finds $\sigma_L(CH_4)/\sigma_L(Ar) = 1.10 \pm 0.005$ for all temperatures considered. Figure 2 also shows that of course the CO_2 molecule is not conformal to Ar and CH_4. The higher steepness of

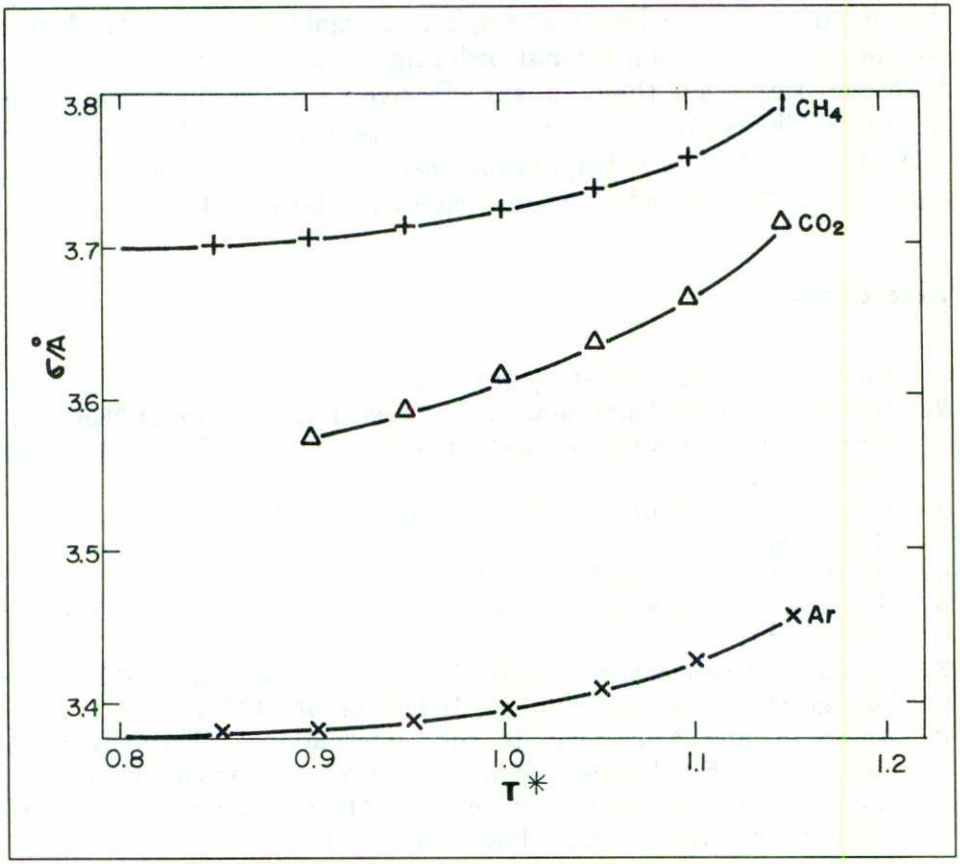

FIGURE 2. Effective diameters for real substances along saturated liquid states. The lines through the points are graphical interpolations.

$\sigma_L(CO_2)$, which is due to its density dependence, arises from the non-sphericity of the CO_2 molecule according to the MCS [1]. From a Lennard-Jones (LJ) fitted to the 2nd virial coefficient of CO_2 one finds $r_m = 4.95$ Å $r_m(CH_4)$ but in Fig. 2 $\sigma_L(CO_2) < \sigma_L(CH_4)$. The values found for $\sigma_L(CO_2)$ at liquid densities are also small when compared with the LJ $r_0 = 4.42$ Å, obtained for the diluted CO_2 gas. These inconsistencies are only apparent and are explained by the different shapes of the CH_4 and CO_2 molecules. The larger density dependence of σ for linear and spherical molecules [1], introduced by the increased orientational ordering of the linear molecules at high densities, make them appear effectively smaller than at gas-like densities. This explanation is confirmed by a simple calculation: for CO_2, the low density extrapolation (using the two-term virial) gives $\sigma_0(CO_2) = 4.35$ Å which is quite close to the LJ $r_0 = 4.42$ Å.

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