
M. J. Maeso and J. R. Solana

Received June 20, 1994

A theoretically based corresponding-states principle is developed for the equation of state of hard-convex-body fluids. For all the fluids considered, the excess compressibility factor, reduced by means of a parameter which can be determined analytically, lies on a single curve whose analytical expression can be obtained from the equation of state of the hard-sphere fluid.

KEY WORDS: equation of state; corresponding states; hard-convex-body fluids; hard spheres.

1. INTRODUCTION

As is well-known, the corresponding-states principle establishes that, for similar substances, the equation of state can be put in the form

\[ p_r = f(T_r, V_r) \tag{1} \]

where subindex \( r \) indicates a reduced quantity and \( f \) is a common function for all these substances. Generally the reducing quantities are the critical constants, so that \( p_r = p/p_c \), \( T_r = T/T_c \), and \( V_r = V/V_c \). Although a simple analytical expression for the function \( f \) has not been derived, experimental evidence has shown that the principle is obeyed by many substances, for which the plots of reduced thermodynamic quantities lie on a single curve.

However, many other substances deviate markedly from this principle. Apart from quantum effects in certain substances and the polarity of the molecules in others, the reason for this deviation is the considerable departure of many molecules from spherical shape. Thus, several attempts have been made...
been made to extend the corresponding-states principle by including one additional parameter that accounts for the effect of the nonsphericity of the molecules. Particularly fruitful has been the acentric factor $\omega$, defined by [1, 2]

$$\omega = -\log p_r - 1.000$$

where $p_r$ is the reduced vapor pressure at $T_r = 0.7$. Then the extended corresponding-states principle is expressed in the form

$$p_r = f(T_r, V'_r, \omega)$$

In this paper, we derive a corresponding-states principle for hard-convex-body (HCB) fluids (see Fig. 1) in terms of a theoretically determined parameter defining the shape of the molecules.

2. THEORETICAL BASIS

The virial theorem for a one-component HCB fluid can be expressed as [3]

$$Z^{HCB} = 1 + \frac{1}{4} \rho (S + 4\pi R^2) \sigma uv g^{uv}(0)$$

Fig. 1. Several of the geometrical shapes considered. Tridimensional bodies are obtained from the rotation of these planar figures around the axis denoted by dashed lines. Left: Prolate (top) and oblate (bottom) spherocylinders. Right: Prolate (top) and oblate (bottom) ellipsoids of revolution. The parameters characterizing the geometry of the molecules are $\gamma = L \sigma$ for spherocylinders, and $\kappa = a/b$ for ellipsoids of revolution. For hard—Gaussian—overlap molecules the shape is not well defined, but they behave rather similarly to ellipsoids of revolution and are characterized also by the aspect ratio $\kappa$. 