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Modeling of n-alkanes and refrigerants with a hard convex body chain equation of state

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ABSTRACT

In this work an equation of state which was previously given for the hard convex body chain molecules was modeled to n-alkanes and refrigerants. The equation of state parameters and the application ranges of density and temperature were determined through fitting with the experimental data. It was found that the collision diameter and the nonspherical geometry parameter are temperature dependent and the relations were also given for their temperature dependencies. The compressibility factor, the reduced bulk modulus and the reduced isobaric expansion coefficient were calculated using the obtained parameters and compared with their experimental values. It was shown that the errors in the properties prediction are within experimental uncertainty. The results show that the equation of state is applicable for alkanes and refrigerants in both subcritical and supercritical region, but the error increases a little in the region away from the critical point.

1. Introduction

Chain molecules such as polymers and proteins, have played a very significant role in the development of human life (Choi et al., 2011; Heller, 1993). Polymeric compounds have chain molecular structure that exhibit different behaviors in different conditions in comparison with materials (Shimanouchi and Mizushima, 1955). Numerous studies have been carried out experimentally on chain molecules by polymer science and technology researchers (Richardson-Burns et al., 2007). However, the experimental studies on different materials are time consuming and the possibility of finding accurate thermodynamic data in the required conditions is almost impossible due to practical problems and a variety of errors. Therefore, the exact equations of state that could quickly obtain thermodynamic data with a minimum of errors would be very valuable. In addition, the equations of state help to determine the properties of materials that cannot be experienced.

Different equations of state have been obtained by different methods for chain molecules. Some of these methods are scaled particle theory (SPT) (Gibbons, 1969; Reiss and Casberg, 1974), analysis of third and fourth Virial coefficients (Bannerman et al., 2010), and thermodynamic perturbation theory (Banaszak et al., 1993; Gross and Sadowski, 2001; Karakatsani et al., 2005). The concept of hard sphere repulsion has been frequently used in the modeling of real fluids. The first hard body equation of state which is based on SPT theory, was given by Gibbons (Gibbons, 1969). Chiew (Chiew et al., 2000) used this concept to show a useful equation of state for polymer liquids. Statistical associating fluid theory (SAFT) equation of state, first time was formulated by Chapman et al. (Chapman et al., 1989) based on the thermodynamic perturbation theory of Wertheim (Wertheim, 1987) for associating chain fluids. Ghonasgi and Chapman (Ghonasgi and Chapman, 1994) were developed an equation of state from the thermodynamic perturbation theory that requires only the contact values of the hard sphere and hard disphere site–site correlation functions as inputs. Although this equation of state has not formulated recently, but due to its high accuracy in predicting of fluids properties it has improved and developed using various methods (Nezbeda, 1997; Shukla and Chapman, 2000).

In spite of the nonspherical geometry of fluids components, the hard sphere model is frequently used in theoretical studies on fluids. However, it seems that the equations of state that consider anisotropy effects can better describe such systems.

Some equations of state for non-spherical molecules have been formulated using Virial equation (Monson and Rigby, 1978; Nezbeda, 1976). An equation of state was also proposed on the basis of the third and fourth Virial coefficients analysis of hard convex bodies by Boublik (Boublik, 1981). The principle of corresponding state has also been used as a method for obtaining the equation of state of non-spherical molecules (Ambrose and Patel, 1984; Elliott et al., 1990). An accurate equation of state for hard convex bodies has been provided by Carnahan and Starling

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Nomenclature

B : Bulk modulus
B_r : Reduced bulk modulus
$g_{HS}(\sigma)$: Hard sphere correlation function
$g_{HCB}(\sigma)$: Site -site correlation function of the hard convex bodies
m : Monomers number of a chain molecule
R : Hard convex body average radius
R^2 : Coefficient of determination
S : Hard convex body curvature area
S_{HCB} : Real surface area of a hard convex body
$S_{HS}(equi)$: Surface area of a hard sphere with the equivalent volume to the hard convex body
S_R : Ratio of S_{HCB} to $S_{HS}(equi)$
V : Hard convex body volume
Z : Compressibility factor
Z_{HSC} : Compressibility factor of a hard sphere chain
Z_{HS} : Compressibility factor a hard sphere
Z_{HCBC} : Compressibility factor of a hard convex body chain
Z_{HCB} : Compressibility factor of a hard convex monomer

Greek letters
α : Nonspherical geometry parameter
α : Isobaric expansion coefficient
α_r : Reduced isobaric expansion coefficient
α_i : Constants of Eq. (6)
σ : Hard sphere diameter
σ_i : Constants of Eq. (7)
η : Packing fraction
κ_T : Isothermal compressibility
ρ : Numerical density

(Carnahan and Starling, 1969). Generalization of this equation to mixtures showed that it can be concluded easily from radial distribution function resulted from SPT theory (SOLANA, 1998). Nezebda et al. (Nezbeda et al., 1979) proposed a universal equation of state for the fluid of hard bodies an arbitrary shape. Song and Mason (Song and Mason, 1990a, b) formulated the equations of state for isotropic fluid of hard convex bodies. A hard convex body equation of state for pure fluids were extended into the mixtures by Barrio and Solana (Barrio and Solana, 1999). Maeso and Solana (Maeso and Solana, 1994) obtained an equation of state for the fluids of the hard convex molecules using the pressure equation and the hard sphere fluid equation of state. The equations of state were also proposed for hard dumbbells by Boublik and Boublik and Nezbeda (Boublík, 1988; Boublik and Nezbeda, 1977). Boublik used the Kihara potential in the statistical mechanical description of systems composed of non-spherical convex molecules and proposed a first-order perturbation theory for such systems (Boublik, 1976; Boublík, 1974). Moreover, the second-order perturbation theory of convex-molecule fluids with pair interactions of the generalized Kihara type is also considered by Boublik (Boublík, 1987). Torikai (Torikai, 2012) was derived an equation of state for parallel rigid spherocylinders by two different routes.

It is clear that, a chain of hard convex bodies is a better representation of the real molecular chain geometry than the hard sphere model. Sadus (Sadus, 1999) formulated a new equation of state for a chain of hard convex bodies by deriving a chain contribution from the hard convex body equation of state which was previously given by Boublik (Boublik, 1981). Determination of the molecular chain properties composed of nonspherical parts was the goal of this formulation. The accuracy of this equation of state has not been investigated for real materials and only the chains of oblate and prolate spherocylinder convex bodies were considered for modeling. Therefore, a question arises about the applicability of the equation of state for real molecules that this work intends to answer.

Apart from ammonia and carbon dioxide, refrigerants are divided into groups according to their chemical composition as: chlorofluorocarbons (CFC), hydrochlorofluorocarbons (HCFC), hydrofluorocarbons (HFC), fluorocarbons (FC), perfluorocarbons (PFC), and hydrocarbons (HC).

Ozone depletion potential (ODP) and Global warming potential (GWP) which is also known as “greenhouse effect” are two environmental issue to get international focus. All refrigerants have GWP. CFCs and HCFCs contain the chlorine and referred to as ozone depleting substances, but HFCs are refrigerants contain no chlorine and are not harmful to the ozone layer, however, they are flammable and their impact on global warming is very large compared with CFC and HCFC refrigerants. HCs (e.g. propane, butane) are environmental burden (no ODP and low GWP) and FC and PFC are fully halogenated fluorocarbons that do not contribute to the depletion of the ozone layer, however, scientists worry that PFCs can contribute to global warming since they have a very high GWP.

Refrigerant gases are used in climate control in commercial and business facilities such as warehouses, stores and office buildings. The refrigerants used in commercial heating, ventilating and air conditioning or regular air conditioning units include HCFCs, CFCs, and PFCs.

In the United States, the Environmental Protection Agency (EPA) has set strict standards for regulating and monitoring a refrigerant leak. EPA’s current regulations require that persons servicing, maintaining, repairing, or disposing of air-conditioning and refrigeration equipment conduct their work in a manner that reduces emissions of ODS. These requirements are now extended to cover these activities, as appropriate, to non-ozone depleting substances that are not exempt from the venting prohibition, which includes HFCs. In addition to expanding coverage to include certain non-ozone depleting substances, the new rule also strengthens existing regulations. The new leak rates are 30 percent for industrial process refrigeration, 20 percent for commercial refrigeration appliances, and 10 percent for comfort cooling and other appliances. These new leak rates are also expanded to cover equipment using HFCs and other substitute refrigerants that are not exempt from the venting prohibition.

In present work, we attempt to investigate the application range of the Sadus equation of state for different states of n-alkanes (HC) and some refrigerants (CFC, HCFC, HFC, and PFC). In this regard, after describing the theoretical foundations of the Sadus equation of state in part 2, the equation parameters were determined by fitting the P-v-T experimental data with the equation of state in part 3 and the application range of pressure, temperature and density for both alkanes and refrigerants was investigated using the obtained parameters. In order to evaluate the equation of state ability in prediction of some properties of alkanes and refrigerants, the calculated compressibility factor using the Sadus equation of state was compared with Tait and Benedict–Webb–Rubin equations of state. The reduced bulk modulus, and the reduced isobaric expansion coefficient were calculated using the determined equation of state parameters and the deviation percent of the predicted properties from the experimental values were investigated. The conclusion of this work was given in part 4.

2. Hard convex body chain equation of state

The primary structure of the hard convex body chain compressibility factor was taken from the hard sphere chain compressibility factor that was developed based on Werthim’s thermodynamic perturbation theory (Wertheim, 1987). According to this theory,