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Cubic and quartic hard-sphere and Lennard-Jones chain equations of state as foundations for complex fluid modeling

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ABSTRACT

Hard-sphere compressibility factor Z and hard-dimer radial distribution function at contact $g_{HD}(\sigma)$ are fit to simple packing fraction η expressions and are used in the dimer version of Wertheim's perturbation theory to obtain five cubic equations of state (EOS's) for athermal hard-sphere chain fluids. The predicted Z^m versus η for various chain lengths m and the reduced second-virial coefficient versus m are compared with simulation data and the original noncubic dimer perturbation theory EOS's. A cubic analog of the Boublik–Mansoori–Carnahan–Starling (BMCS) EOS successfully represents the unlike pair correlation function $g_{12}(\sigma)$ and Z versus η for binary hard-sphere mixtures of moderate size difference in the components. The new CTPT-D models are extended to calculate Z^m versus η for binary homonuclear hard-sphere chain mixtures. The choice of a suitable EOS dispersion term to simultaneously represent single phase *PVT* and phase equilibria is briefly explored. A similar TPT approach was used to derive a quartic EOS for Lennard-Jones chain fluids, and Z^m versus η isotherms are determined and compared with simulation results for chains up to 100 segments long. The new cubic and quartic EOS's provide a simple foundation for developing equations of state for complex fluids including multipolar and association effects.

1. Introduction and background

Simple and accurate equations of state (EOS's) are desirable for chemical process design. On one hand, several empirical van der Waals-type cubic equations of state with a few meaningful parameters and three well-defined molar volume roots are frequently used [1–5]. However, application of these EOS's at extreme conditions in temperature and/or pressure or to systems with hydrogen-bonding species is problematic. In contrast, theoretically-based equations of state that isolate molecular effects including repulsion, dispersion, multipolar interactions and covalent and hydrogen bonding have more recently emerged [5,6]. The most successful of these models are the statistical associating fluid theory (SAFT) type of EOS's [6–8], which have greatly improved the accuracy of phase behavior description for all types of pure fluids and mixtures, but are computationally intense. SAFT models typically have more than four volume roots, and computational difficulties are sometimes encountered in their application [9,10].

We use two approaches in this paper to leverage the advantages of both empirical cubic and SAFT-type models to develop simple cubic and quartic in molar volume nonpolar chain fluid equations of state as the foundation for complex fluid EOS development. Both methods are applications of Wertheim's thermodynamic perturbation theory (TPT) and use simple packing fraction polynomials; however, the reference fluid is different in each case. The first scheme, known as the dimer perturbation theory TPT-D, uses the hard-dimer reference fluid (information about the hard-sphere fluid is also required); where as the second approach, LJ-TPT1-M, is based on the Lennard-Jones monomer reference fluid.

Fig. 1 depicts a "thought process" for the first TPT approach in which attractive hard-sphere chains are constructed by adding covalent bonds and dispersion interactions to repulsive hard-sphere segments. This paper mainly considers the top route to obtain athermal hard-sphere chains and briefly investigates the left-hand route to form attractive hard-spheres. Another work [11] considers the complete process of constructing attractive hard-sphere chains (bottom right of Fig. 1).

Alternatively, equations of state for model or real chain fluids with simple isotropic attractive forces (dispersion) may be obtained using the Lennard-Jones ("soft-sphere") platform, which offers the advantage of having *built-in* attractive interactions. Here, chain molecules are constructed with *overlapping* spherical

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Nomenclature

a	Parameter in new empirical hard-dimer radial distribution (pair correlation) function
a_{ij}	Parameter in Lennard-Jones monomer pair correlation function [Eq. (47)]
a_{Att}	Dispersion parameter in attractive term [Eqs. (29)–(30)]
a_1	Parameter in Lennard-Jones monomer equation of state [Eq. (46)]
a_2	Parameter in Lennard-Jones monomer equation of state [Eq. (46)]
A	Helmholtz free energy (J/mol)
A^{Res}	Residual Helmholtz free energy (J/mol)
b	Parameter in new empirical hard-dimer radial distribution (pair correlation) function
b_1	Parameter in Lennard-Jones monomer pair correlation function at contact value [Eq. (49)]
b_2	Parameter in Lennard-Jones monomer pair correlation function at contact value [Eq. (49)]
b_3	Parameter in Lennard-Jones monomer pair correlation function at contact value [Eq. (49)]
B	Second-virial coefficient ($\mathrm{m^3/mol}$)
c	Molecular parameter ($\pi m \sigma^3 N_{\mathrm{Av}}/6$) ($\mathrm{m^3/mol}$)
$f(V)$	Function of molar volume defined by Eq. (36) ($\mathrm{bar\,m^{12}/mol^4}$)
$f'(V)$	Derivative function of molar volume defined by Eq. (37) ($\mathrm{bar\,m^9/mol^3}$)
$F_{11}(x)$	Composition function for hard-sphere component 1
$F_{22}(x)$	Composition function for hard-sphere component 2
$g_{\mathrm{HD}}(\sigma)$	Hard-dimer radial distribution (pair correlation) function at contact value
$g_{\mathrm{HS}}(\sigma)$	Hard-sphere radial distribution (pair correlation) function at contact value
$g_{ii}(\sigma)$	Like i–i pair correlation function at contact value
$g_{ij}(\sigma)$	Unlike i–j pair correlation function at contact value
$g_{\mathrm{LJ}}(\sigma)$	Lennard-Jones monomer pair correlation function at contact value
k	Boltzmann constant (1.381×10^{-23} J/K)
K	Sphere size ratio
m	Number of segments
N_{AV}	Avogadro's number ($6.02 \times 10^{23}\ \mathrm{mol^{-1}}$)
P	Absolute pressure (bar)
P_{Exp}	Experimental absolute pressure (bar)
P^{Sat}	Vapor pressure (bar)
P^*	Lennard-Jones reduced pressure
r	Distance between Lennard-Jones segments (m)
R	Universal gas constant ($8314\ \mathrm{m^3\,bar/mol\,K}$)
T	Absolute temperature (K)
T_{Exp}	Experimental absolute temperature (K)
T^*	Lennard-Jones reduced temperature
V	Fluid molar volume ($\mathrm{m^3/mol}$)
V_{Exp}	Experimental fluid molar volume ($\mathrm{m^3/mol}$)
V^{l}	Liquid molar volume ($\mathrm{m^3/mol}$)
V^{v}	Vapor molar volume ($\mathrm{m^3/mol}$)
x_i	Mole fraction of component i
Y	Dispersion compressibility factor [Eq. (29)] or modified dispersion compressibility factor [Eq. (30)]
Z	Compressibility factor
Z_{Chain}	Covalent bonding compressibility factor contribution
Z_{Dis}	Dispersion compressibility factor
Z_{Exp}	Experimental compressibility factor
Z_{HS}	Hard-sphere (repulsive) compressibility factor
Z_{LJ}	Compressibility factor of Lennard-Jones monomer fluid
Z^m	Compressibility factor of hard-sphere chain of length m segments
$Z_{\mathrm{LJ}}{}^m$	Compressibility factor of Lennard-Jones chain fluid

Greek symbols

β	New EOS universal parameter (1.17)
$\beta(T^*)$	Lennard-Jones quartic EOS parameter at T^*
ε	Lennard-Jones energy parameter (J)
φ	Fugacity coefficient
φ^{l}	Liquid fugacity coefficient
φ^{v}	Vapor fugacity coefficient
δ	New EOS universal parameter (3.4188)
$\Gamma_{\mathrm{LJ}}(r)$	Potential energy between two Lennard-Jones segments (J)
η	Molecular packing fraction [defined by Eqs. (4), (13), (27) and (44)]
ρ	Number density of hard-spheres ($\mathrm{m^{-3}}$)
ρ^*	Lennard-Jones reduced density
σ	Hard-sphere (segment) diameter (m)
σ_i	Hard-sphere (segment) diameter of component i (m)
σ_{ii}	Hard-sphere (segment) diameter of component i (m)
σ_{ij}	Effective hard-sphere (segment) diameter of an i–j pair (m)
σ_{LJ}	Lennard-Jones size parameter (m)
ζ_2	Two-dimensional fluid packing fraction for hard-sphere mixture [defined by Eq. (21)]
ζ_3	Three-dimensional fluid packing fraction for hard-sphere mixture [defined by Eq. (22)]

Subscripts

1	Parameter 1 in Eq. (46) or (49)
2	Parameter 2 in Eq. (46) or (49)
3	Parameter 3 in Eq. (49)
11	Like pair (component 1)
22	Like pair (component 2)
12	Unlike pair (components 1 and 2)
Av	Avogadro's
Chain	Chain (or covalent bonding)
Dis	Dispersion
Exp	Experimental value
FCC	Face-centered cubic
HD	Hard-dimer
HS	Hard-sphere
i	Component i
i	Iteration i
j	Component j
ii	Like pair (component i)
ij	Unlike pair (components i and j)
jj	Like pair (component j)
LJ	Lennard-Jones

Superscripts

i	Index in Eq. (47) or (48)
j	Index in Eq. (47) or (48)
l	Liquid value
m	Number of segments
Res	Residual property
Sat	Saturated value
v	Vapor value
*	Reduced value