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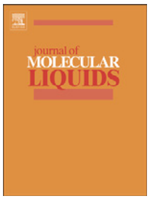

Unified SAFT-VR theory for simple and chain fluids formed of square-well, triangular-well, Sutherland and Mie segments

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ABSTRACT

The thermodynamic properties of simple and chain fluids, whose molecules interact through the three following basic hard-core intermolecular potentials: the square-well (SW), the triangular-well (TW) and the Sutherland (SU) $[-\varepsilon(d\,/\,r)^{\gamma}]$ potentials are presented in a unified mathematical framework. In order to achieve this goal we use the Barker–Henderson perturbation theory with the macroscopic compressibility approximation (BH-MCA) of monomer fluids combined to a simple, analytic expression of the hard-sphere radial distribution function (RDF) derived by Sun [Can. J. Phys. 83 (2005) 55], which allows the first-order perturbation term of the Helmholtz free energy, f_1, to be obtained in terms of the same generic analytic function for the three potentials. This function depends on three parameters which assume different values according to the potential considered. Other thermodynamic quantities such as the compressibility factors can be derived from f_1, which thus plays a pivotal role in the equation of state (EOS) obtained from perturbation theory. Numerical values of f_1 obtained from this generic function are in good agreement with recent Monte Carlo simulations for the three aforementioned basic potentials, as well as with the various parameterizations of f_1 in terms of an effective packing fraction η_{eff} for the square-well and Sutherland potentials commonly used in the statistical associating fluid theory for potentials of variable range (SAFT-VR). For the corresponding chain fluids, Wertheim first-order thermodynamic perturbation theory (TPT1) is used. It requires the SAFT-VR expressions of the potentials RDF at the hard-core contact d, g(d), and its derivative with respect to the packing fraction, which can be expressed in terms of the generic function giving f_1. Numerical values of g(d) are also in agreement with the corresponding Monte Carlo results. The equations of state (EOS) of the SW, TW and SU chain fluids are then obtained in simple, analytical forms. The above three basic potentials can then be combined to give more complicated molecular interactions. One important example of combination is studied. It involves the linear combination of two Sutherland potentials with $\gamma = \alpha, \beta$ to obtain the Mie(α,β) class of interactions, of which the Lennard–Jones LJ(12,6) or Mie(12,6) is a particular example. Numerical values of: a) the Mie(12,6) first-order perturbation term of the residual Helmholtz free energy, f_1^{Mie}, b) the radial distribution function at contact, $g^{\text{Mie}}(\sigma)$, $[u^{\text{Mie}}(\sigma) = 0]$, and c) the reduced pressure or compressibility factor of the monomer, dimer and tetramer Mie(12,6) fluids, obtained from the generic function, f_1, corresponding to the combined Sutherland potentials, are compared to Monte Carlo and molecular dynamics simulations and to the recent enhanced SAFT-VR Mie 20013 EOS of Lafitte et al. [J. Chem. Phys. 139 (2013) 154504], whose improvements with respect to the previous SAFT-VR Mie 2006 EOS are highlighted in detail. The results obtained from the generic function f_1 are slightly more accurate for the Mie(12,6) monomer fluid, while the results from Lafitte et al., which uses a new f_1 parameterization of η_{eff} for the Sutherland potentials, valid for $5 < \gamma \leq 100$, are more accurate for the Mie(12,6) dimer and tetramer fluids.

1. Introduction

One of the main goals of Statistical Mechanics is to understand how the microscopic properties of matter such as molecular interactions influence its macroscopic properties. The development of accurate models for the thermodynamic properties of complex fluids with chainlike molecules (e.g., polymers, alkanes, and surfactants) is essential in process design calculations, which to be efficient requires moreover accurate as well as simple, analytic algebraic expressions. As a result considerable effort has been dedicated to the development of analytic molecular-based equations of state (EOS), in which the parameters are directly related to the microscopic properties of the molecules.

One of the most successful theories for such EOS is the statistical associating fluid theory (SAFT), of which there are many excellent reviews [1–3]. In this article we shall concentrate on one of the most popular versions of the theory: the variable range type called SAFT-VR [4–7]. It

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was first developed for chain molecules composed of monomer segments interacting with hard-core potentials [4], u*(r) = u(r) / ε, of diameter d, depth − ε, and with the following variable attractive tails expressed in terms of the reduced intermolecular distance x = r / d as

a) The square-well potential SW(λ) (Fig. 1):

$$\begin{aligned} &= +\infty, && x<\lambda, \\ u^*(x) = u(x)/\varepsilon &= -1, && 1<x<\lambda, \\ &= 0, && x>\lambda. \end{aligned} \tag{1}$$

b) The Sutherland potential SU(γ) (Fig. 1):

$$\begin{aligned} u^*(x) &= +\infty, && x<1, \\ u^*(x) &= -x^{-\gamma}, && x>1, \end{aligned} \tag{2}$$

and also the hard-core Yukawa potential (YU(γ): u*(r) = −exp [−γ(x − 1)] / x, x > 1). The theory can then be generalized to soft-core systems by linearly combining several SU(γ) [4] potentials. When two SU(γ) potentials are used, one obtains the important Mie(α,β) potentials (γ = α, β), of which the Lennard–Jones LJ(12,6) is a well-known particular case.

In the SAFT-VR theory the residual (res) Helmholtz free energy for associating chain molecules $F_c^{res} = F_c - F_c^{id}$ (the superscript id means ideal gas and the subscript c means chain), from which other thermodynamic functions can be derived, are divided into three independent parts:

$$\frac{F_c{}^{res}}{N_c k_B T} = \frac{F_c - F_c{}^{id}}{N_c k_B T} = \frac{F^{mono}}{N_c k_B T} + \frac{F^{chain}}{N_c k_B T} + \frac{F^{assoc}}{N_c k_B T}. \tag{3}$$

F^{chain} and F^{assoc} are respectively the contribution due to chain formation and intermolecular association. Both quantities are evaluated within the framework of Wertheim first-order thermodynamic perturbation theory (TPT1) [8,9]. N_c is the number of chain molecules in volume V, and k_B is the Boltzmann constant. F^{mono} is the residual free energy of monomer segments calculated from the high-temperature Barker–Henderson (BH) perturbation expansion [10–17] as

$$\frac{F^{mono}}{Nk_B T} = \frac{F^{HS}}{Nk_B T} + \frac{F_1}{Nk_B T}\frac{1}{T^*} + \frac{F_2}{Nk_B T}\frac{1}{T^{*2}} = \frac{F^{HS}}{Nk_B T} + \frac{f_1}{T^*} + \frac{f_2}{T^{*2}}, \tag{4}$$

where $N = m_c N_c$ is the number of monomers in volume V, m_c is the number of monomers in a chain molecule, $T^* = k_B T / \varepsilon$ is the reduced temperature, F^{HS} is the hard-sphere (HS) free energy given by its Carnahan–Starling (CS) expression in terms of the packing fraction $\eta_d = \pi\rho_d^* / 6 = \pi\rho d^3 / 6$ ($\rho = N / V$ is the monomer density and $\rho_d^* = \rho d^3$) as.

$$\frac{F^{HS}}{Nk_B T} = \frac{4\eta_d - 3\eta_d{}^2}{(1-\eta_d)^2} \tag{5}$$

The first-order term is given by

$$\frac{F_1}{Nk_B T} = f_1 = 12\eta_d \int_1^\infty g^{HS}(x) u^*(x) x^2 dx, \tag{6}$$

while the second-order term in the macroscopic compressibility approximation (MCA) [12] may be expressed as

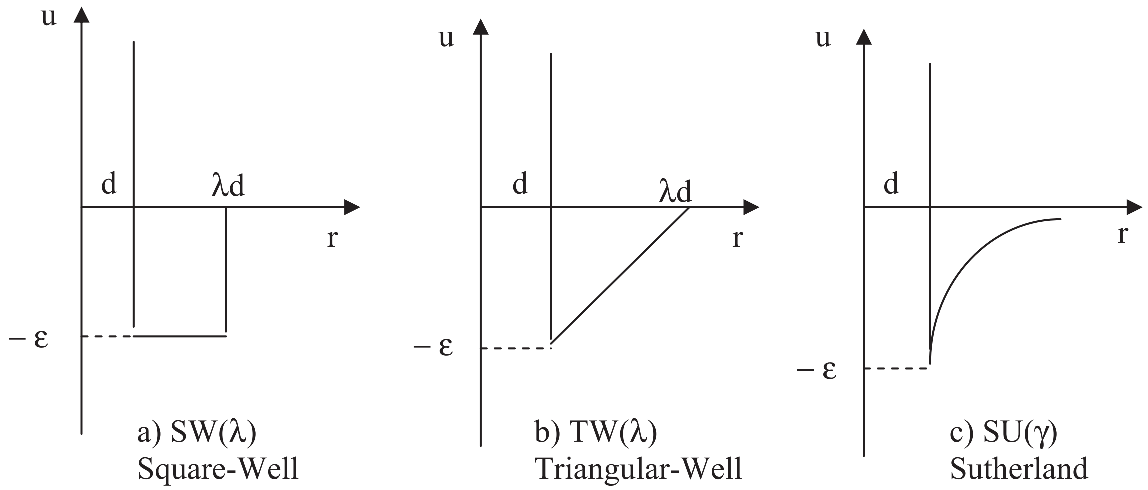
$$\frac{F_2}{Nk_B T} = f_2 = -6\eta_d K^{HS} \int_1^\infty g^{HS}(x) \left[u^*(x)\right]^2 x^2 dx, \tag{7}$$

$$K^{HS} = \frac{(1-\eta_d)^4}{1 + 4\eta_d + 4\eta_d{}^2 - 4\eta_d{}^3 + \eta_d{}^4}, \tag{8}$$

where $g^{HS}(x)$ is the hard-sphere radial distribution function (HS-RDF) and K^{HS} is the HS isothermal compressibility given by its CS expression [18].

Different analytical formulae are used for the free energies, F^{mono}, corresponding to the three aforementioned potentials. They are obtained by applying first the mean-value theorem to the monomer free energy perturbation terms f_1 and f_2 to factorize the function $g^{HS}(x)$ out of the integration sign and then use its Carnahan–Starling (CS) expression at contact for an effective packing fraction η_{eff}. This expression of f_1 is then employed to obtain the monomer cavity function at contact with the hard core, y(d), required for the calculation of F^{chain} [4]. In this paper we do not consider the calculation of F^{assoc}.

For example for the SW(λ) potential, a first set of analytical formulae was derived in this way for λ ≤ 1.8 by Gil-Villegas et al. [4], and a second set was later proposed to extend this range up to λ = 3 by Patel et al. [19]. For the SU(γ) potential a first set was proposed by Gil-Villegas et al. [4] valid only for 3 < γ ≤ 12; this restricted the SU potentials which could be combined to give Mie potentials. For this reason a second set of formulae was recently proposed by Lafitte et al. [6] in an enhanced version of the SAFT-VR theory, which extended the range of γ to 5 < γ ≤ 100. Finally, another set of analytical formulae was also proposed for the YU(γ) potential with 1.1 ≤ γ ≤ 4 [4]. This great variety of analytical formulae comes from the use of the mean-value theorem, which introduces different average distances ξ at which the HS-RDF



a) SW(λ)
Square-Well

b) TW(λ)
Triangular-Well

c) SU(γ)
Sutherland

Fig. 1. Three basic intermolecular potentials with hard-core diameter d of liquid theory: a) the square-well SW(λ) potential; b) the triangular-well TW(λ) potential and c) the Sutherland SU(γ) potential.