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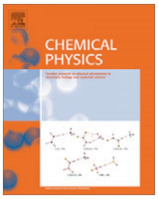

Second virial coefficients of Exp-6 chains: A Monte Carlo simulation

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ABSTRACT

The second virial coefficients of Exp-6 chains are calculated using the Monte Carlo method. The results are presented as the scaled second virial coefficient $B_2/(m^2\sigma^3)$ for various chain lengths m and repulsive-wall steepness parameters α at different scaled temperatures T^*. The scaled coefficient reduces and converges to a constant value as $m \to \infty$. Interestingly, the scaled coefficient scales as $B_2/(m^2\sigma^3) \propto -\alpha^{-1}$, where the dependence reduces for larger m. The gyration radius increases with α, and in good solvent regime, scales like a self-avoiding chain when $m \to \infty$. The interaction energy between two chains depends on m, T^*, and α. With increasing m, the interaction becomes less repulsive. With increasing α or T^*, the repulsion between chains increases, and chains behave as they are in good solvent conditions. Moreover, the θ point decreases with increasing α and reducing m. Finally, the results are compared with the theoretical predictions using the PHSC model.

1. Introduction

There have been long-standing theoretical and experimental efforts on characterizing the osmotic pressure of polymeric solutions. Generally, two different approaches have been developed for the theoretical derivation of the osmotic pressure [1]: one uses a discrete model leading to the lattice theory and the other a continuum model, which is based on either the McMillan–Mayer theory or the pair correlation function inhered in the simple theory of liquids. The McMillan–Mayer theory highlights an analogy between the virial expansion of the osmotic pressure and gas pressure. Thus, the cornerstone of the theoretical osmotic pressure derivation is to calculate virial coefficients.

At low enough pressure and density, the leading coefficient for the specification of the gas pressure is the second virial coefficient B_2, where this quantity is equivalent to the osmotic second virial coefficient of a polymeric solution A_2 as long as the segment–segment interactions of chain fluids are specified by a solvent-mediated potential model.

In last two decades, there have been extensive molecular -simulation and theoretical studies for describing chain fluids with various segment–segment interaction potential models, such as hard-sphere, square-well, and Lennard–Jones (LJ) [2–5]. However, there exists limited study on Exp-6 or modified-Buckingham chain fluids [6], mainly arising from the relatively complex form of the Exp-6 potential model for molecular simulations and theoretical treatments compared with the other foregoing potential models.

Even though the LJ model, which has a simple form, describes the nonbonded interaction energy fairly well at moderate experimental conditions, but it fails at high enough pressure and densities (for example, see [7]). In spite of some simulations studies [29], the Exp-6 model is believed to be more realistic than the LJ model for describing the non-bonded interaction energy, and this apparently complex potential model proves successful in describing the properties of fluids compared to the LJ model at high enough pressure and density, and over wide ranges of pressure and temperature [6,8–11]. Moreover, the Exp-6 potential model is becoming increasingly interested for modeling phase equilibria and transport properties of fluids (see [12,13] and references therein). In parallel, there have been increasing interest in potential models such as Mie (n − 6), which has the same number of parameters as the Exp-6 potential model [33,30,32].

A successful method, even though computationally expensive, for the determination of B_2 of chain fluids is using the Monte Carlo (MC) method. References [14–16,3,17] presented B_2 of, respectively, hard-sphere, square-well, and LJ chain fluids using the Monte Carlo method. However, in recent years, the modeling of chains is becoming increasingly atomistic [18]. Even though, these atomistic models do not require the classical assumptions inhered in idealized models, but the analytical investigation of these atomistic models are not as easy and clean as idealized models. Also, simulating idealized models provide guidelines for developing more accurate and realistic theories.

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Here, we present the second virial coefficient of Exp-6 chains by the MC method, and we compare the theoretical predictions of the coefficient with the MC values. The remainder of this work is outlined as follows. In Section 2, the potential model and the Monte Carlo method are described. In Section 3, the results are presented, and we use PHSC (Perturbed Hard Sphere Chain Theory) model to obtain the second virial coefficients of Exp-6 chains theoretically, and then compare the results with the simulation values. Concluding remarks are presented in Section 4.

2. The potential model and the Monte Carlo method

2.1. The potential model

In our work, each chain is considered as consisting of m segments linearly connected by rigid bonds with the bond-length σ, which is assumed to be unit. The non-bonded interaction energy u between two nonadjacent segments in a chain or between two segments of two different chains is quantified by the modified-Buckingham or Exp-6 potential model with the following form (for a historical review on the derivation of this potential model, see [19])

$$u(r) = \begin{cases} \infty & r \leqslant \lambda r_m \\ \frac{\epsilon}{1-\frac{6}{\alpha}}\left\{\frac{6}{\alpha}\exp\left[\alpha\left(1-\frac{r}{r_m}\right)\right] - \left(\frac{r_m}{r}\right)^6\right\} & r > \lambda r_m \end{cases}, \tag{1}$$

where r the distance between two segments, α the repulsive-wall steepness parameter, r_m the distance between two segments at which the energy of attraction is maximum, *i.e.* the distance at which $\frac{\partial u}{\partial r}|_{r=r_m} = 0$ and u is negative, ϵ the maximum energy of attraction occurring at the separation r_m, and λr_m the distance at which Eq. (1) goes through a false maximum, *i.e.* the distance at which $\frac{\partial u}{\partial r}|_{r=\lambda r_m} = 0$ and u is positive. The value of λ is the smallest root of $\lambda^6 \exp[\alpha(1-\lambda)] = 0$ [20]. In the limit $\alpha \to \infty$, the Exp-6 potential reduces to the following equation which, in principle, is the Sutherland potential model,

$$u(r) = \begin{cases} \infty & r \leqslant r_m \\ -\epsilon\left(\frac{r}{r_m}\right)^6 & r > r_m. \end{cases} \tag{2}$$

Following the foregoing method, the values of λ and r_m for various values of α = 15, 30, 100, and ∞ are presented in Table 1. However, analytical expressions for r_m and λ as a function of α are reported in the literature [10].

Fig. 1 highlights the influence of the repulsive wall steepness α on the potential energy between two interacting segments. Evidently, with increasing α, the repulsion between segments enhances. There are various simulation studies on the effect of α on thermodynamic properties and phase equilibria of Exp-6 fluids including, the work of [11] highlighting the reduction of the temperature range over which vapor–liquid coexistence is observed, and the work of [8] highlighting the larger α, the harder is an Exp-6 fluid.

2.2. The Monte Carlo method

Table 1
Values of λ and r_m for various values of α.

α	λ	σ/r_m
15	1.682455×10^{-1}	0.894170
30	1.465604×10^{-2}	0.932341
100	6.248806×10^{-7}	0.970041
∞	–	1.00

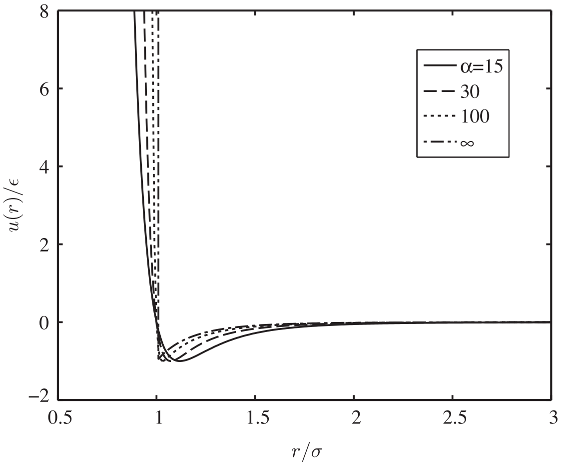

Fig. 1. The scaled segment–segment potential versus the distance for various α = 15, 30, 100, and ∞.

The equation of state is expressed using the virial expansion as

$$\frac{P}{\rho k_B T} = 1 + B_2\rho + B_3\rho^2 + \cdots, \tag{3}$$

where P is the pressure, ρ the density, T the absolute temperature, k_B the Boltzmann constant, B_2 the second virial coefficient, and B_3 the third virial coefficient. For spherically symmetric molecules, where the intermolecular potential energy U depends only on the intermolecular distance r, B_2 is [7]

$$B_2 = 2\pi \int_0^\infty [1 - e^{-U(r)/(k_B T)}] r^2 dr. \tag{4}$$

For polyatomic or complex molecules, the potential energy not only depends on the distance between molecules centers, but also is a function of the orientations and conformations of the molecules. In such cases, the second virial coefficient is [21,1]

$$B_2 = \frac{\int e^{-U_1(\Omega_1)/(k_B T)} e^{-U_2(\Omega_2)/(k_B T)} [1 - e^{-U_{12}(R_{12})/(k_B T)}] dR_{12} d\Omega_1 d\Omega_2}{2\int e^{-U_1(\Omega_1)/(k_B T)} d\Omega_1 \int e^{-U_2(\Omega_2)/(k_B T)} d\Omega_2}, \tag{5}$$

where $U_1(\Omega_1)$ and $U_2(\Omega_2)$ are the intramolecular energies, $U_{12}(R_{12})$ the intermolecular potential, Ω_1 and Ω_2 the conformations of the two molecules, and R_{12} the distance between the centers of mass of the two molecules. The second virial coefficient for polyatomic or complex molecules cannot be determined with common integration methods because of high dimensional integral inhered in Eq. (5). The most efficient method to perform the integration is using the Monte Carlo method.

Few MC methods have been developed for evaluating the virial coefficients, including parallel tempering (see [17], and references therein), Mayer-Sampling (see [18], and references therein), grand canonical (see [22], and references therein), and a classical method utilizing pivot [19,23] or reptation algorithm [16].

Here, we use the classical MC method for calculating the second virial coefficient of Exp-6 chains through Eq. (5). For this purpose, single chain conformations are produced by the pivot algorithm [19]. In the pivot algorithm, a trial conformation is generated by randomly choosing a segment as the pivot point, and by rotating the shorter end of the chain around the pivot point. The new generated conformation is accepted with the probability $\min\{1, \exp[-(E_2 - E_1)/(k_B T)]\}$, where E_1 and E_2 are the intramolecular potential energies of the chain old and trial conformations, respectively. Thus, two distinct sets of single chain conformations are generated. Then, the average intermolecular energy is calculated as follows; two conformations, one from each set, are placed at a random configuration, say, i at a given distance between the two chains centers of mass R_{12}, *i.e.* they placed at randomly chosen