CROATICA CHEMICA ACTA CCACAA **67** (1) 143–148 (1994)

ISSN 0011-1643
CCA–2171

Original Scientific Paper

Padé Approximants to the Equation of State of Hard Sphere Mixtures

Branko Borštnik

National Institute of Chemistry, Hajdrihova 19, 61000 Ljubljana, Slovenia

Received October 04, 1993

The values of the fifth viral coefficients, which were reported in our previous work on hard sphere mixtures with additive diameters at the diameter ratio $\sigma_2/\sigma_1 = 0.6$. were used in order to construct a Padé approximant to the equation of state. The methodology was developed for constructing Padé approximants for binary mixtures when only low order viral coefficients are available. The resulting approximants exhibit satisfactory accuracy when compared with a linear combination of the results of Percus Yevick and the mean spherical approximation, or with the results of computer simulation.

INTRODUCTION

The equation of state (EOS) of the one-component hard sphere fluid is known fairly accurately.[1] The most reliable are the results of computer simulation. Other standard approaches are virial expansion, Padé approximants and various approaches based on integral equations for the pair correlation function. These methods reproduce the exact results within a pro mill of relative error. The situation is less favourable in the case of mixtures of hard spheres. Some results of computer simulations[2] as well as results of integral equation theories[3,4] and virial expansion[4,5,6] are available.

As far as the results of virial expansion are concerned, the sets of second, third and fourth coefficients were evaluated by various authors for a limited number of ratios of hard sphere diameters.[5] In our previous work,[7] we calculated the set of the fifth viral coefficient for $\sigma_2/\sigma_1 = 0.6$.

In this work, we present the methodology for constructing the Padé approximants for the equation of state of binary mixtures. We also present the numerical results showing that Padé approximants, which are constructed on the basis of the first five sets of viral coefficients, can compete with other theoretical approaches.

CONSTRUCTION OF PADÉ APPROXIMANTS

Padé numerical schemes[8] were successfully applied to the one-component hard sphere fluid. The best known example is the Carnahan-Starling equation[9,10]

$$\frac{\beta p}{\rho} = \frac{(1+\eta+\eta^2-\eta^3)}{(1-\eta)^3}$$

where $\beta = 1/kT$, ρ is the number density and $\eta = \pi\rho/6$ is the packing fraction. The above mentioned approximation results if the virial coefficients in the series $\beta p/\rho = 1 + B_2\eta + B_3\eta^2 + B_4\eta^3 + \ldots$ are expressed as $B_i = 3\cdot(i-1) + (i-1)^2$ and the summation is carried out. In the literature one can also find other, more accurate Padé approximants of the EOS of one component fluid.[8,11]

In our previous work, we presented the results of the virial expansion of EOS for a two-component mixture of hard spheres with additive diameters for $\sigma_2/\sigma_1 = 0.6$. It turned out that, at higher densities, the absence of terms beyond the fifth power of density introduces a substantial error. Due to the fact that the essence of the usefulness of the Padé approximants lies in the possibility of partial reconstruction of the sum with high order terms missing, we decided to design Padé approximants for the EOS of binary mixtures of hard spheres.

In general, the Padé approximants are constructed in the form of the quotient of two polynomials $\beta p/\rho = P_1(\rho)/P_2(\rho)$. The coefficients of the polynomials are determined by the requirement that the quotient of the polynomials should fit the virial expansion. This procedure does not have a unique solution since one can freely choose the order of the polynomials P_1 and P_2. The number of the coefficients defining P_1 and P_2 may not exceed the number of known coefficients in the virial series. Further, the density can be scaled arbitrarily and we introduce parameter γ by means of the relation $\eta = \gamma\rho$. The virial coefficients depend upon γ in the following way

$$B_i^{(\gamma)} = B_i/\gamma^{i-1} \tag{1}$$

where B_i are the virial coefficients that appear in virial expansion in terms of the number of particles per σ^3. If one chooses $\gamma = \pi/6$, then $\gamma\rho$ represents the packing fraction. We considered γ as a variational parameter that becomes fixed in the process of construction of Padé approximants. As far as determination of the polynomials $P_1^{(\gamma)}$ and $P_2^{(\gamma)}$ is concerned, we did not follow the standard approach. Due to the successful role of the Carnahan – Starling approximative equation of state of the pure hard sphere fluid, we decided to follow the procedure in which the coefficients of polynomials $P_1^{(\gamma)}$ and $P_2^{(\gamma)}$ are determined in such a way that four known virial coefficients are fitted to a cubic parabola that contains four unknown parameters $\alpha_0^{(\gamma)}$ through $\alpha_3^{(\gamma)}$.

$$B_{i+1}^{(\gamma)} = \alpha_0^{(\gamma)} + \alpha_1^{(\gamma)}\, i + \alpha_2^{(\gamma)}\, i^2 + \alpha_3^{(\gamma)}\, i^3 \tag{2}$$

The unknowns $\alpha_k^{(\gamma)}$ can be determined by solving the system of four linear equations (2). The solution has the following form:

$$\begin{aligned}
\alpha_0^{(\gamma)} &= (48B_2^{(\gamma)} - 72B_3^{(\gamma)} + 48B_4^{(\gamma)} - 12B_5^{(\gamma)})/12 \\
\alpha_1^{(\gamma)} &= (-52B_2^{(\gamma)} + 114B_3^{(\gamma)} - 84B_4^{(\gamma)} + 22B_5^{(\gamma)})/12 \\
\alpha_2^{(\gamma)} &= (18B_2^{(\gamma)} - 48B_3^{(\gamma)} + 42B_4^{(\gamma)} - 12B_5^{(\gamma)})/12 \\
\alpha_3^{(\gamma)} &= (-2B_2^{(\gamma)} + 6B_3^{(\gamma)} - 6B_4^{(\gamma)} + 2B_5^{(\gamma)})/12
\end{aligned} \tag{3}$$

Provided that $\alpha_i^{(\gamma)}$ are known, on the basis of Eq. (2), one can also express all higher virial coefficients. If they are inserted into the virial series, the summation can be carried out and the following equation results

$$\beta p/\rho = [1 + (\alpha_0^{(\gamma)} + \alpha_1^{(\gamma)} + \alpha_2^{(\gamma)} + \alpha_3^{(\gamma)} - 4)(\gamma\rho) + (-3\alpha_0^{(\gamma)} - 2\alpha_1^{(\gamma)} + 4\alpha_3^{(\gamma)} + 6)(\gamma\rho)^2 + \\ + (3\alpha_0^{(\gamma)} + \alpha_1^{(\gamma)} - \alpha_2^{(\gamma)} + \alpha_3^{(\gamma)} - 4)(\gamma\rho)^3 + (1 - \alpha_0^{(\gamma)})(\gamma\rho)^4]/[(1-\gamma\rho)^4] \quad (4)$$

This equation reproduces, for example, the Carnahan Starling equation if one chooses $\gamma = \pi/6$, $\alpha_0 = 0$, $\alpha_1 = 3$, $\alpha_2 = 1$ and $\alpha_4 = 0$.

The methodology described above can be easily implemented when constructing the Padé approximants for the pure one-component fluid. We also applied it in the case of mixtures where the virial equation of state looks as follows

$$\beta p/\rho = 1 + [x_1^2 B_{11}^{(\gamma)} + 2x_1x_2 B_{12}^{(\gamma)} + x_2^2 B_{22}^{(\gamma)}]\gamma\rho + \\ + [x_1^3 B_{111}^{(\gamma)} + 3x_1^2x_2 B_{112}^{(\gamma)} + 3x_1x_2^2 B_{122}^{(\gamma)} + x_2^3 B_{222}^{(\gamma)}](\gamma\rho)^2 + \dots \quad (5)$$

where x_1 and x_2 are the mole fractions $x_1 = \rho_1/(\rho_1 + \rho_2)$; $x_2 = 1 - x_1$. If the virial expansion defined in this equation is written for a fixed value of mole fractions, then each square bracket attains a fixed value $B_i^{(\gamma)}(x)$, which can be evaluated by means of known sets of virial coefficients. Since these sets are known for $i = 2$ to $i = 5$, one can determine all four parameters $\alpha_k(x)$ and, subsequently, the coefficients of the polynomials entering in (4).

RESULTS AND DISCUSSION

In Table I, the four sets of virial coefficients from various sources are given for $\sigma_2/\sigma_1 = 0.6$. When the virial series in the form given by Eq. (5) are evaluated at a specific value of the mixing ratio, one obtains the values of $B_i^{(\gamma)}(x)$ for $i = 2$ to 5, which can be inserted into (3) to get $\alpha_k^{(\gamma)}$ values that define the pressure through (4). Calculations were performed for all meaningful γ values. The resulting pressure was

TABLE I

Virial coefficients for the binary mixture of hard spheres at the diameters ratio $\sigma_1/\sigma_2 = 0.6$. The coefficients are expressed in terms of σ_1^3 for the expansion when the density is expresssed in terms of particles per σ_1^3. The sets of second and third coefficients can be obtained in a straightforward way, the fourth coefficients are taken from Ref. 5 and the fifith ones from Ref. 7.

B_{11} 2.094	B_{12} 1.072	B_{22} 0.4523			
B_{111} 2.7415	B_{112} 1.0718	B_{122} 0.3825	B_{222} 0.1279		
B_{1111} 2.6356	B_{1112} 0.9121	B_{1122} 0.2805	B_{1222} 0.0891	B_{2222} 0.02656	
B_{11111} 2.121	B_{11112} 0.654	B_{11122} 0.20	B_{11222} 0.0584	B_{12222} 0.0172	B_{22222} 0.00462

compared with the results of computer simulation and with the results of the linear combination of Percus – Yevick and the mean spherical approximation of Zhou and Stell.[4] It appears that the latter method quite satisfactorily reproduces the computer simulation results and is convenient because it provides the compressibility data on the entire interval of densities and mixing ratios. The calculations were performed for the points of ρ_1 and ρ_2 lying on the isochores of the effective density

$$\eta(x) = \gamma(\rho_1\sigma_1^3 + \rho_2\sigma_2^3) = \gamma(\rho_1 + \rho_2)\,(x_1\sigma_1^3 + x_2\sigma_2^3) \tag{6}$$

The results are depicted in the figures. As far as the γ dependence is concerned, we found that the best agreement with the above mentioned reference results is obtained with $\gamma = 0.515$ and all the results refer to this value. The value is very close to $\gamma = \pi/6 = 0.5236$, where the effective density η represents the packing fraction. Figure 1 presents the effective values of the virial coefficients as functions of the mixing ratio. In Figure 2, the $\alpha_k^{(\gamma)}$ and $a_i^{(\gamma)}$ are plotted. $a_i^{(\gamma)}$ are the coefficients of polynomial $P_1(\eta)$. In Figure 3, the compressibility factor $\beta p/\rho$ is plotted for four isotherms of the effective density. For comparison, we also plot Zhou and Stell approximation and virial expansion with the virial coefficients up to the fifth one. We can see that, at low density values, all the results are nearly indistinguishable. However, at high density values, the result of the Padé approximation is much better than the virial expansion. Comparison of Figures 1 and 3 indicates that the x_1 dependence of the compressibility factor is directly related to the x_1 dependence of virial coefficients $B_i^{(\gamma)}(x)$. On the other hand, variation of $\alpha^{(\gamma)}$ and $a^{(\gamma)}$ values is rather unpredictable.

There are reasonable chances that, in the near future, the set of sixth virial coefficients will be evaluated for binary mixtures of hard sphere. In that case, it would be possible to produce even more accurate Padé approximants.

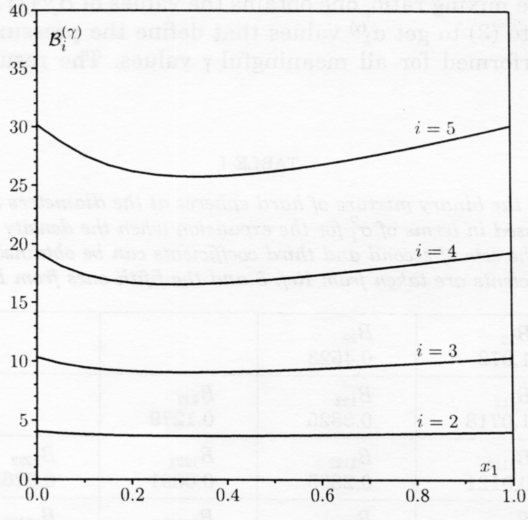

Figure 1. The x_1 dependence of the effective virial coefficients for $\gamma = 0.515$ and $\sigma_2/\sigma_1 = 0.6$.

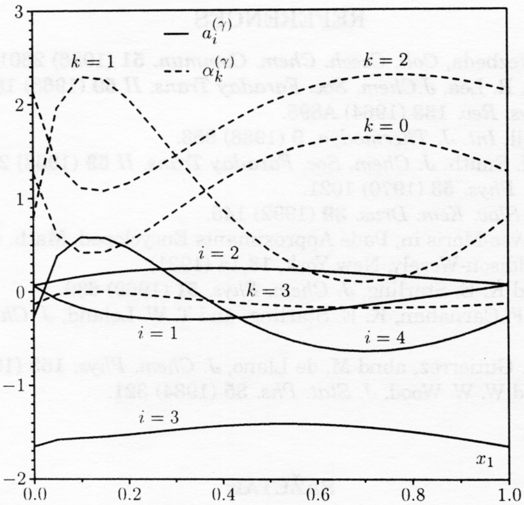

Figure 2. The x_1 dependence of the parameters $\alpha^{(\gamma)}$ (see Eq. (2)) and the cofficients $a^{(\gamma)}$ of the Padé polynomial $P_1(\eta)$ as given Eq. (4). The value of γ is 0.515.

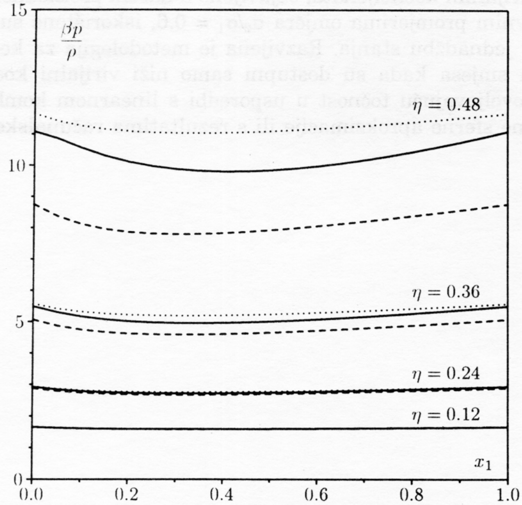

Figure 3. Compressibility factor ($\beta p/\rho$) as a function of the mixing ratio for hard sphere binary mixtures with the diameters ratio $\sigma_2/\sigma_1 = 0.6$. The curves are drawn at a fixed value of the effective density (Eq.(6)) as marked in the Figure. $\gamma = 0.515$. Solid line: our Padé approximants; dashed lines: virial expansion up to the fifth term; dotted line: the results of Zhou and Stell, which are the best numerical approximation to the exact results provided by computer simulation.

Acknowledgement. – The work was supported by the Ministry of Science and Technology of the Republic of Slovenia. A. Borštnik and D. Lukman are acknowledged for the help in programming.

REFERENCES

1. T. Boublik and I. Nezbeda, *Coll. Czech. Chem. Commun.* **51** (1986) 2301.
2. E. B. Smith and K. R. Lea, *J.Chem. Soc. Faraday Trans. II* **59** (1963) 1535.
3. J. L. Lebowitz, *Phys. Rev.* **133** (1964) A895.
4. Y. Zhou and G. Stell, *Int. J. Thermodyn.* **9** (1988) 953.
5. M. Rigby and E. M. Smith, *J. Chem. Soc. Faraday Trans. II* **59** (1963) 2469.
6. M. Rigby, *J. Chem. Phys.* **53** (1970) 1021.
7. B. Borštnik, *Vestn. Slov. Kem. Drus.* **39** (1992) 145.
8. G. A. Baker, P. Graves-Moris in, Padé Approximants Encycloped. Math. and its Applications G. C. Rota (Ed), Addison-Wesely, New York, **13,14** (1981).
9. N. F. Carnahan and K. E. Starling, *J. Chem. Phys.* **51** (1969) 639.
10. G.A. Mansoori, N. F. Carnahan, K. E. Starling, and T. W. Leland, *J. Chem. Phys.* **54** (1971) 1523.
11. G. A. Baker, Jr., G. Gutierrez, abnd M. de Llano, *J. Chem. Phys.* **153** (1984) 283.
12. J. J. Erpenbeck and W. W. Wood, *J. Stat. Phs.* **35** (1984) 321.

SAŽETAK

Primjena Padéove aproksimacije na jednadžbu stanja smjese neproničnih kugli

Branko Borštnik

Vrijednosti petih virijalnih koeficijenata, objavljene u našem prethodnom radu o smjesi nepronične kugli s aditivnim promjerima omjera σ_2/σ_1 = 0.6, iskorištene su u konstrukciji Padeove aproksimacije za jednadžbu stanja. Razvijena je metodologija za konstrukciju Padéove aproksimacije binarnih smjesa kada su dostupni samo niži virijalni koeficijenti. Dobivena aproksimacija ima zadovoljavajuću točnost u usporedbi s linearnom kombinacijom rezultata Percus Yevica i prosječne sferne aproksimacije ili s rezultatima računalske simulacije.