

## STATISTICAL MECHANICAL TEST OF MHEMHS MODEL OF THE INTERACTION THIRD VIRIAL COEFFICIENTS

ESAM Z. HAMAD and G. ALI MANSOORI

*Department of Chemical Engineering, University of Illinois, (Box 4348) Chicago, IL 60680 (U.S.A.)*

KENNETH R. HALL

*Department of Chemical Engineering, Texas A&M University, College Station, TX 77843 (U.S.A.)*

(Received October 9, 1987; accepted in final form March 2, 1988)

### ABSTRACT

Hamad, E.Z., Mansoori, G.A. and Hall, K.R., 1988. Statistical mechanical test of MHEMHS model of the interaction third virial coefficients. *Fluid Phase Equilibria*, 43: 205–212.

The proposed MHEMHS model for the interaction third virial coefficients by McGregor et al. is tested using statistical mechanical expressions for these coefficients. The reasons for its accuracy in different ranges of temperature and density is investigated.

### INTRODUCTION

The virial equation of state is one of the few equations for real fluids which has a sound theoretical basis from statistical thermodynamics. When truncated after the third virial coefficient, the virial equation of state provides an adequate representation of the behavior of gases up to about 2/3 of the critical density. To apply this equation of state to mixtures requires the second and third cross virial coefficients, which represent interaction between unlike molecules.

The cross second virial coefficients are known exactly for conformal potentials, but this is not the case for the cross third virial coefficients. A number of approximations which allow calculation of the cross third virial coefficients from pure component third virial coefficients have been proposed. However, those approximations are not accurate at low temperatures where the pure component coefficients are negative. Even at higher temperatures the accuracy of predicting the cross coefficients is low when the interacting molecules differ significantly in molecular size and energy.

## THEORY AND CALCULATIONS

Recently McGregor et al. (1987) have proposed a relation among the cross third virial coefficients. For binary mixtures, this relation is

$$3C_{ijj} - 2C_{iii} - C_{jjj} = 3C_{iij} - C_{iii} - 2C_{jjj} \quad (1)$$

where  $C_{iii}$  and  $C_{jjj}$  are the pure component third virial coefficients and  $C_{iij}$  and  $C_{ijj}$  are the cross coefficients. For multicomponent mixtures, eqn. (1) takes the form

$$3C_{ijk} - C_{iii} - C_{jjj} - C_{kkk} = \frac{1}{2}(\delta C_{ij} + \delta C_{ik} + \delta C_{jk}) \quad (2)$$

where  $\delta C_{ij} = 3C_{iij} - 2C_{iii} - C_{jjj}$ . For ideal solutions, the  $\delta C_{ij}$ s are all identically zero. When the McGregor, Holste, Eubank, Marsh, Hall and Schouten (MHEMHS) approximation is substituted in the truncated virial equation, it takes the following form:

$$Z = 1 + \rho \sum_{i=1}^n \sum_{j=1}^n x_i x_j B_{ij} + \rho^2 \left( \sum_{i=1}^n x_i C_{iii} + \sum_{i=1}^n \sum_{j=i+1}^n x_i x_j \delta C_{ij} \right) \quad (3)$$

where  $Z$  is the compressibility factor (real gas factor),  $\rho$  is the density,  $n$  is the number of components in the mixture,  $x_i$  is the mole fraction of component  $i$  and  $B_{ij}$  is the second virial coefficient of the pair  $ij$ . The quantities  $\delta C_{ij}$  ( $i = 1, n; j = 1, n$ ) must be evaluated from experimental data for one binary mixture for each pair of chemical species.

The MHEMHS approximation was used to calculate the compressibility factor of a number of real fluid mixtures (McGregor et al., 1987). The results for binary, ternary and quaternary systems, when compared to the experimental data, showed a very high accuracy in predicting the compressibility factor. The error is  $\leq 0.1\%$  in all cases.

In this work the MHEMHS approximation is studied from the point of view of statistical mechanics. This can be done in two ways: imposing eqn. (1) on a model potential and investigate the implications of doing so, or comparing both sides of eqn. (1) when they are calculated from the exact expressions of  $C_{ijk}$ .

To test the implications of imposing eqn. (1) on a model potential, the cross third virial coefficients of hard-sphere and square-well potentials are utilized. The interaction coefficients for the hard-sphere model potential are known exactly. For binary mixtures they are (Kihara, 1943, 1955)

$$C_{112} = (2\pi N_0/3)^2 [\sigma_{11}^6 - 18\sigma_{11}^4\sigma_{12}^2 + 32\sigma_{11}^3\sigma_{12}^3]/24 \quad (4)$$

$$C_{122} = (2\pi N_0/3)^2 [\sigma_{22}^6 - 18\sigma_{22}^4\sigma_{12}^2 + 32\sigma_{22}^3\sigma_{12}^3]/24 \quad (5)$$

Substituting eqns. (4) and (5) into eqn. (1) produces

$$4(r^3 - 1)x^3 - \frac{9}{4}(r^4 - 1)x^2 - \frac{1}{2}(r^6 - 1) = 0 \quad (6)$$

where  $x = \sigma_{12}/\sigma_{22}$  and  $r = \sigma_{11}/\sigma_{22}$ . When  $r$  is different from unity, eqn. (6) becomes

$$x^3 - \frac{9}{16}(r^4 - 1)/(r^3 - 1)x^2 - \frac{1}{8}(r^3 + 1) = 0 \quad (7)$$

Equation (7) may be viewed as an equation which provides the combining rule for  $\sigma_{12}$ . The real  $\sigma_{12}$  combining rule of hard spheres is the arithmetic mean of  $\sigma_{11}$  and  $\sigma_{22}$

$$\sigma_{12} = (\sigma_{11} + \sigma_{22})/2$$

This expression will provide us with a reference to which the accuracy of the MHEMHS approximation can be judged.

Equation (7) is cubic in  $x$ . It can be shown that it has only one real root for  $r \geq 0$ . This root is

$$\sigma_{12}/\sigma_{22} = [a^3 + b + Q^{1/2}]^{1/3} + [a^3 + b - Q^{1/2}]^{1/3} + a \quad (8)$$

where  $a = \frac{3}{16}(r^4 - 1)/(r^3 - 1)$ ,  $b = \frac{1}{16}(r^3 + 1)$  and  $Q = 2a^3b + b^2$ .

Equation (8) is the  $\sigma_{12}$  combining rule for which the MHEMHS approximation is exact for a mixture of additive hard spheres. This means that although the hard spheres are additive,  $\sigma_{12} = (\sigma_{11} + \sigma_{22})/2$ , one needs to use a biased combining rule in the MHEMHS model in order to get the correct cross third virial coefficients for additive hard spheres. As  $r$  approaches unity the combining rule given by eqn. (8) approaches the arithmetic mean. Even at values of  $r$  far from unity, eqn. (8) predicts values of  $\sigma_{12}$  close to the arithmetic mean. For example, at  $r = 0.5$ , which corresponds to a ratio of the pure components closest-packed volumes of  $1/8$ , the error in predicting  $\sigma_{12}$  by eqn. (8) is about 8%. This error reflects in an even smaller value of 1.7% in the compressibility factor compared to that calculated using the arithmetic mean at  $\rho\sigma_{22}^3 = 0.35$  for equimolar mixture. At  $r = 0.9$  the error in the compressibility factor is 0.1%.

For non-additive hard spheres, or non-additive pair potentials in general, the same procedure illustrated above can be used to find the biased combining rule that will give the correct cross third virial coefficients with the MHEMHS model.

A similar calculation can be performed for a mixture of square-well fluids. The square-well potential is

$$u_{ij}(r) \begin{cases} \infty & r < \sigma_{ij} \\ -\epsilon_{ij} & \sigma_{ij} < r < \lambda\sigma_{ij} \\ 0 & r > \lambda\sigma_{ij} \end{cases} \quad (9)$$

The cross third virial coefficients for this potential have been derived by Kihara (1943, 1955). The combining rule for size is the arithmetic mean.

However, unlike the hard-sphere fluid, the virial coefficients for a square-well fluid are temperature dependent. Imposing eqn. (1) then implies that  $\sigma_{12}$  depends upon temperature in addition to  $\sigma_{11}$ ,  $\sigma_{22}$ ,  $\epsilon_{11}$  and  $\epsilon_{22}$ . When testing the MHEMHS approximation for this fluid one must know the critical properties to make sure that the comparison is performed in the gas phase. For a pure square-well fluid with  $\lambda = 1.5$ , Alder and Wainwright (1960) obtained the following values of the critical constants from molecular dynamics simulation:

$$kT_c/\epsilon = 1.28, \quad v_0/v_c = 0.235$$

where  $v_0$  is the closest-packed volume. It is estimated that for  $kT/\epsilon_{22} \geq 1.75$  and for  $\epsilon_{11}/\epsilon_{22} \leq 1.5$  the mixture is in the gaseous state. The compressibility factor calculation is performed at two temperatures,  $kT/\epsilon_{22} = 1.75$  and 2.0, for three values of the molecular energy parameters ratio,  $\epsilon_{11}/\epsilon_{22} = 0.5, 1.0$  and 1.5, and at two densities,  $\rho\sigma_{22}^3 = 0.35$  and 0.7.

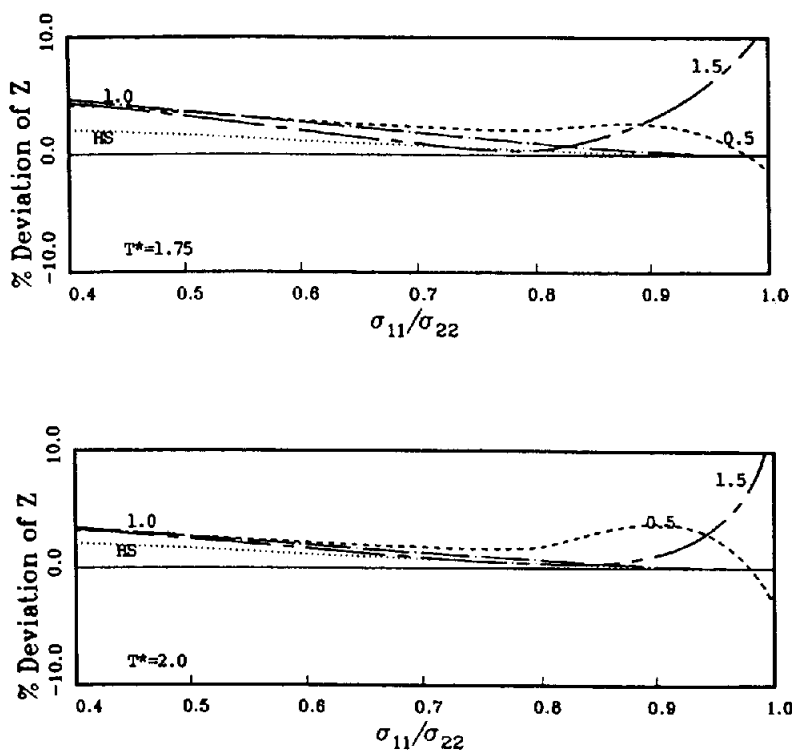


Fig. 1. The error in predicting the compressibility factor as a function of the molecular size ratio,  $\sigma_{11}/\sigma_{22}$ , for additive hard-sphere (HS) and square-well equimolar mixtures when the cross third virial coefficients are calculated from the MHEMHS approximation. The numbers on the curves are the values of the molecular energy ratio,  $\epsilon_{11}/\epsilon_{22}$ , for square-well fluids (the hard-sphere potential has no energy parameter). The mixtures are at a reduced density,  $\rho\sigma_{22}^3$ , of 0.35 and reduced temperatures,  $kT/\epsilon_{22}$ , of 1.75 and 2.0.

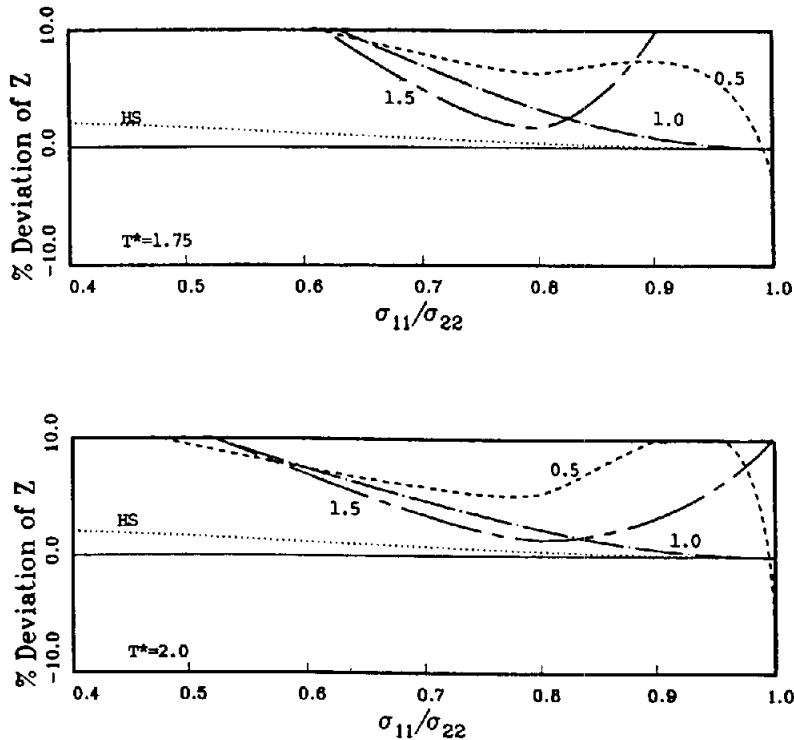


Fig. 2. The error in predicting the compressibility factor as a function of the molecular size ratio,  $\sigma_{11}/\sigma_{22}$ , for additive hard-sphere (HS) and square-well equimolar mixtures when the cross third virial coefficients are calculated from the MHEMHS approximation. The numbers on the curves are the values of the molecular energy ratio,  $\epsilon_{11}/\epsilon_{22}$ , for square-well fluids (the hard-sphere potential has no energy parameter). The mixtures are at a reduced density,  $\rho\sigma_{22}^3$ , of 0.70 and reduced temperatures,  $kT/\epsilon_{22}$ , of 1.75 and 2.0.

The error in predicting the compressibility factor of an equimolar mixture of hard spheres with  $\sigma_{12}$  from eqn. (8) appears in Figs. 1 and 2. Similar results are also shown for the square-well fluid. The two figures show that for energy ratio,  $\epsilon_{11}/\epsilon_{22}$ , of unity the error in the square-well fluid compressibility factor is slightly higher than that of the hard-sphere fluid. The effect of changing the energy ratio is more pronounced for molecules with similar sizes. The temperature has a moderate effect on the error, but the qualitative behavior remains the same.

Another way of testing the MHEMHS approximation is to calculate both sides of eqn. (1) and compare their values. Following McGregor et al. (1987) the following notation will be used

$$K = 3C_{112} - 2C_{111} - C_{222} = \delta C_{12} \quad (10)$$

$$L = 3C_{122} - C_{111} - 2C_{222} = \delta C_{21} \quad (11)$$

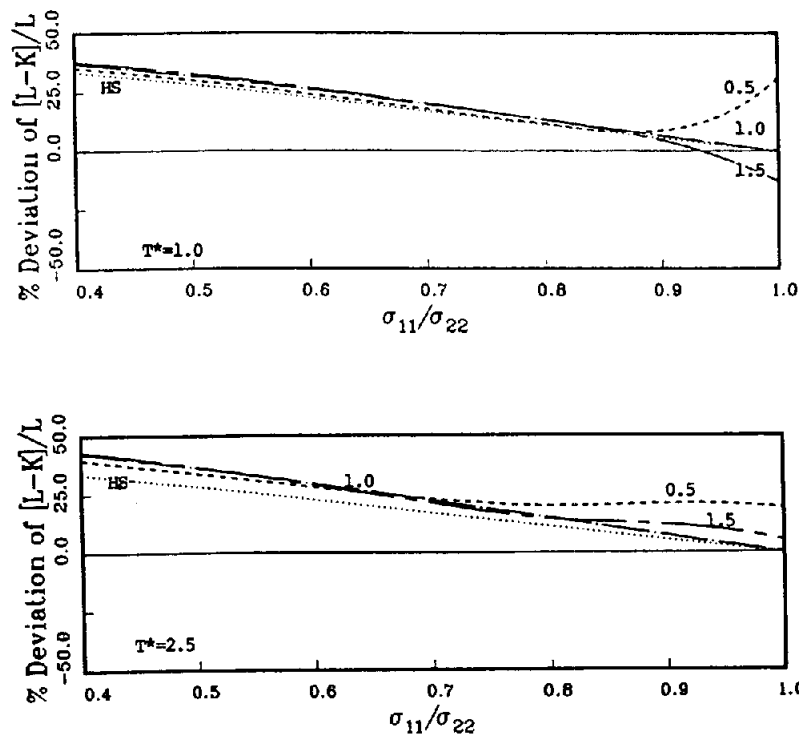


Fig. 3. The deviation between the quantities  $L = 3C_{112} - 2C_{111} - C_{222}$  and  $K = 3C_{221} - 2C_{222} - C_{111}$  for additive hard-sphere (HS) potential and the square-well potential with  $\lambda = 1.5$ . The numbers on the curves are the values of the molecular energy ratio,  $\epsilon_{11}/\epsilon_{22}$ , for the square-well potential (the hard-sphere potential has no energy parameter). The figure demonstrates the relative insensitivity of  $L$  and  $K$  to temperature.

The MHEMHS approximation equates  $K$  and  $L$ . To see how good is this approximation one can calculate the quantities  $K$  and  $L$  from exact model fluid third virial coefficients and compare the two. This comparison has been done for the hard-sphere and the square-well potentials. The results are presented in Figs. 3 and 4 for hard-sphere fluid and for square-well fluid with  $\lambda = 1.5, 2.0$  and  $\epsilon_{11}/\epsilon_{22} = 0.5, 1.0, 2.0$ . The figures show that the error is smallest for molecules with similar values of  $\epsilon$  and  $\sigma$ , as observed before. However, for  $\sigma_{11}/\sigma_{22} = 1$  the values of  $\epsilon_{11}/\epsilon_{22}$  and  $\lambda$  have a dramatic effect on the difference between the quantities  $K$  and  $L$ . This effect dies out as the size difference increases due, possibly, to cancellation of errors. One noticeable feature in the two figures is the small effect of temperature on the deviation between  $K$  and  $L$ . At the higher temperature of  $kT/\epsilon_{22} = 2.5$  the deviation is larger than that at the lower temperature of 1.0, particularly at large size ratios, where the square-well and the hard-sphere deviations

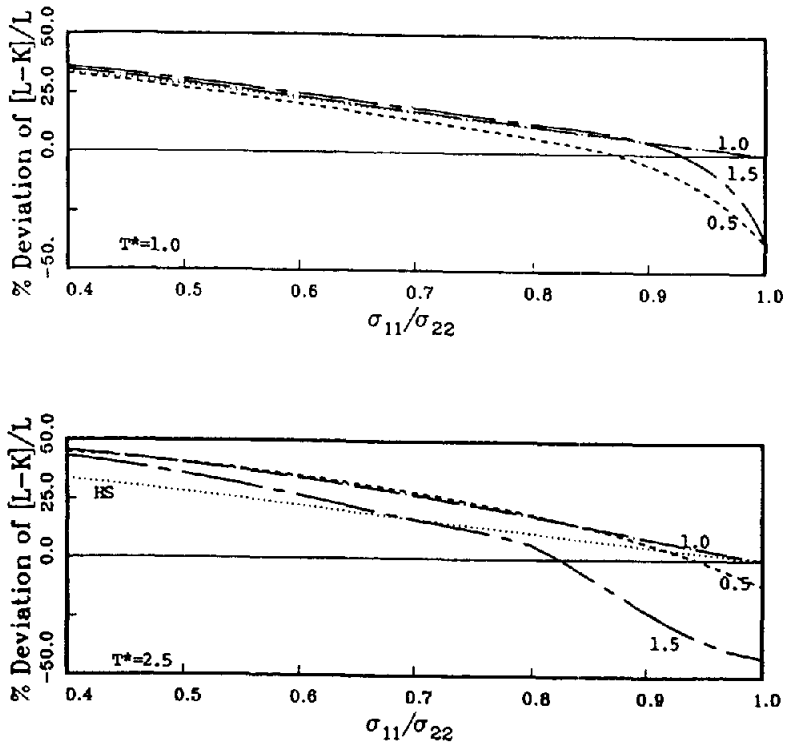


Fig. 4. The deviation between the quantities  $L = 3C_{112} - 2C_{111} - C_{222}$  and  $K = 3C_{221} - 2C_{222} - C_{111}$  for additive hard-sphere (HS) potential and the square-well potential with  $\lambda = 1.8$ . The numbers on the curves are the values of the molecular energy ratio,  $\epsilon_{11}/\epsilon_{22}$ , for the square-well potential (the hard-sphere potential has no energy parameter). The figure demonstrates the relative insensitivity of  $L$  and  $K$  to temperature.

become practically the same. This implies that the energy difference has very small effect on the MHEMHS approximation for molecules with large size differences.

## CONCLUSIONS

The virial equation of state, which is among the few real fluid equations of state with a sound theoretical basis, can be used to get the mixture properties if the cross virial coefficients are known. Statistical mechanics provides expressions for the cross virial coefficients in terms of the potential functions. These expressions are not very useful for real fluids because the potential functions are not known accurately, in addition to the lengthy calculations needed to get the virial coefficients from the statistical mechanical expressions. McGregor et al. (1987) have proposed a simple approxima-

tion which allows calculation of the cross third virial coefficients from the pure fluid coefficients and one binary mixture data point.

In this work we have shown that the proposed relation among the cross third virial coefficients by McGregor et al. (1987) can be made exact by the proper choice of the size combining rule,  $\sigma_{12}$ . The fact that for real fluids the quantity  $\delta C_{ij} = 3C_{iij} - 2C_{iii} - C_{jjj}$ , which is related to  $\sigma_{12}$ , is fitted to the experimental data provides the proper value of  $\sigma_{12}$  at a given temperature. A very important feature of the MHEMHS approximation is the relative insensitivity of  $\delta C_{ij}$  to temperature for a given binary as shown in Figs. 3 and 4. The high accuracy of the MHEMHS approximation is a result of this fact.

#### ACKNOWLEDGEMENTS

This research was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences of the U.S. Department of Energy Grant DE-FG02-84ER13229.

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