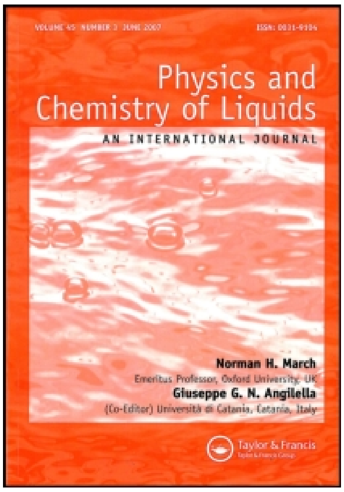

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THERMODYNAMICS OF THE WIDOM–ROWLINSON MODEL. COMPUTER CALCULATION RESULTS COMPARED WITH MEAN FIELD AND PERCUS–YEVICK VALUES

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Recent molecular dynamics (MD) calculations showed that the mean field approximation is to be preferred over the Percus–Yevick one for the prediction of the coexistence curve of the Widom–Rowlinson (WR) mixture model.

Further MD and Monte-Carlo calculations results are presented here for the pressure and the pair correlation function of the WR mixture in a large region of states. The mean field approximations is found to give reasonable agreement with the computer results in a wide density region, while the Percus–Yevick approximation generates nearly exact results at low densities but overestimates the pressure for denser states. This might explain why the Percus–Yevick theory predicts the demixing density too high compared with mean field and exact computer calculation results.

KEY WORDS: Mixtures, mean field, pair correlations, thermodynamics

1 INTRODUCTION

In a recent work it could be shown by molecular dynamics (MD) calculations that the coexistence curve of the Widom–Rowlinson (WR) model is quite well predictable by mean field (MF) and Percus–Yevick (PY) approximation methods[1]. Though these methods gave entirely satisfactory results for this model mixture, the computer calculations revealed that the PY approximation is somewhat inferior to the MF theory in predicting the phase separation. Hence the purpose of the present work was two-fold:

i) detailed comparison of MF, PY and exact MD data for the thermodynamics and the structure of the WR model in order to find reasons for the mentioned deficiencies.

ii) direct comparison of thermodynamics and structure of the 'hard soft sphere' system, which was chosen in Ref. 1 in place of the hard sphere system, and the hard sphere system using MD and Monte-Carlo (MC) computations.

Point (ii) was of interest, because we found in a previous study that the 'hard soft sphere' (HSS) system, whose particles interacted via a $(1/r)^{30}$-term, r being the separation between two particles, represents the genuine hard sphere (HS) system with respect to dynamic quantities to a very good approximation[2]. For static quantitites we expected even better agreement of both systems.

2 MODELS, CALCULATIONS AND STATES

The WR model considers a binary mixture consisting of interacting particles of unlike species and non-interacting particles of the same kind[1]. Originally the interaction was assumed to be that of hard spheres. However, we consider here hard core interaction given by the HS-diameter, σ, as well as 42-HSS interaction according to the following interaction potential expression:

$$u_{\mathrm{HSS}} = \varepsilon\left(\frac{\sigma}{r}\right)^{42},$$

where ε denotes the energy and σ the 'volume' parameter. The chosen set of parameters is listed in Table 1.

MF and PY approximations were used in the form given by Karkheck and Stell[3].

We summarize here solely the final expressions for the compressibility factor and the contact value of the 1–2 pair correlation function.

Denoting the compressibility factor by z and the contact value of the pair correlation function of unlike pairs of particles by g_{12}, we have from the mean field theory:

$$z^{\mathrm{MF}} = P/(nkT) = 1 + nx_1x_2; \; g_{12}^{\mathrm{MF}} = 1,$$

where P denotes the pressure, k the Boltzmann constant, T the temperature, x_1, x_2 the mole fractions and n the total number density of the system. $\sigma^3 = 3/(4\pi)$ is additionally assumed.

The PY approximation yields:

$$z^{\mathrm{PY}} = 1 + \frac{1}{nC_{11}} \sum_{i=1}^{7} C_{ii}(2i - 1)(n^2 x_1 x_2)^i$$

Table 1 Potential parameters.

system	σ (Å)	ε/k (K)
HS	3.405	—
HSS	3.405	119.8

k Boltzmann's constant

Table 2 Technical details of the molecular dynamics and the Monte-Carlo computations.

A. MD	
Particle number	108, 256
Number of integration steps	2×10^4
Integration step	0.5×10^{-14}s
Cut off radius	1.25σ–2.5σ
Ensemble	NVE**p** (*N* number of particles, *V* volume, *E* energy and **p** total momentum of a system)
Integration scheme	Stoermer Verlet
Computation time per 1000 steps (Cyber 205)	8.7s (N = 256)
B. MC	
Particle number	256
Number of MC steps	5×10^6
Acceptance ratio	0.6 0.8
Ensemble	NVT (T temperature; for the HS system meaningless)
Computation time per 10^5 steps (Cyber 205)	8.0s

with

$$C_{11} = -1;\ C_{22} = 0.08095;\ C_{33} = -0.01743$$

$$C_{44} = 0.0058;\ C_{55} = -0.00219;\ C_{66} = 0.00104$$

$$C_{77} = -0.00060.$$

$$g_{12}^{\mathrm{PY}} = \frac{1}{C_{11} n^2 x_1 x_2} \sum_{i=1}^{7} C_{ii}(2i - 1)(n^2 x_1 x_2)^i.$$

These approximations are, of course, only strictly valid for HS systems.

For the HSS-system we performed MD calculations in the common $NVE\mathbf{p}$ ensemble, where N denotes the particle number, V the total volume, E the energy and $\mathbf{p}$ the total momentum of the system. Technical details of the runs are given in Table 2. For the HS-system, MC computations were carried out using the method in detail described by Wood[4]. Some technical advices for these latter calculations are summarized in Table 2. Note, that in the case of hard spheres, the MC computations are particularly simple. The program has only to check overlap events[5].

Compositions of mole fraction 0.5 and 0.75 were considered for comparisons. The density range studied was extended in order to include the homogeneous as well as the inhomogeneous regions of the phase diagram.

3 RESULTS

3.1 Phase separation

Using the method of computing the local mole fractions we determined the lower critical demixing density of the WR HS model by Monte Carlo calculations. The

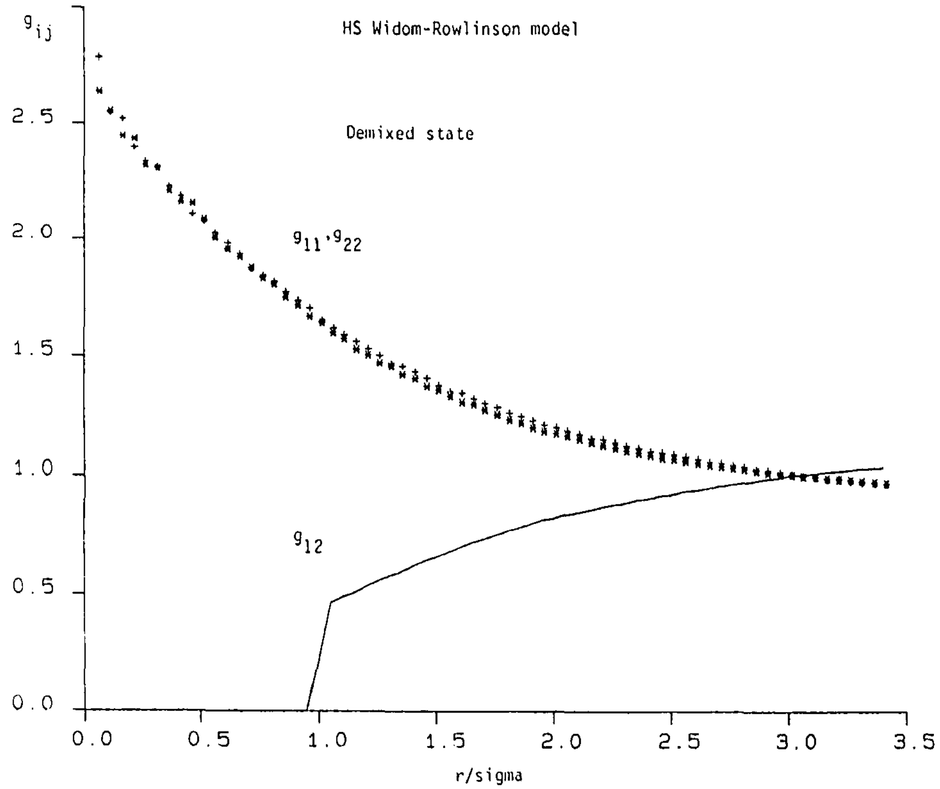

Figure 1 Pair correlation functions of the HS Widom–Rowlinson mixture. Lower curve: $g_{12}(r/\sigma)$. $n^* = 0.7737$.

local mole fraction method is described in detail in Ref. 6, and we therefore omit here a further discussion. For illustration, we show, however, the three pair correlation functions of a predemixed state in the figure. The 'scissors' formed by these functions is typical of a thermodynamically unstable state in the 2-phase region.

The results are listed in Table 3 together with our earlier data of the HSS WR model and those obtained by the MF and the PY approach. We see that the critical demixing density of the HS WR system agrees practically within the error bars with

Table 3 Critical phase separation density of the equimolar Widom–Rowlinson mixture.

n_c^* $\left(\frac{N}{V}\sigma^3\right)$	*calculation method*
0.410 + 0.015	MD (30HSS potential)[x)]
0.45 ± 0.02	MC (HS pot.)
0.5711	PY (HS pot.)
0.4775	MF (HS pot.)

[x)] from Ref. 1.

that determined previously for the HSS WR mixture by MD calculations. The HS system value is little higher than the HSS system value as expected due to the very small but positive range of the HSS potential at separations larger than σ. So the findings of our previous work are here nicely supported.

3.2 Compressibility factor

For equimolar composition of the WR mixture, we have listed the compressibility factor z computed by MD and MC as well as predicted by MF and PY theory for a large range of states in Table 4. The inhomogeneous states predicted by the various calculation methods are indicated. Several things are evident from this table:

i) for all the states, the computer calculation results of the HS and the HSS system agree rather well within about the error bars. There is, however, a tendency of the HSS values to fall above the HS values, as expected

ii) for homogeneous states, there is good agreement between the computer results and MF and PY predictions. The MF compressibility factors exceed, however, systematically slightly those of the PY theory and the computer calculations, while the PY method generates nearly exactly the Monte Carlo results.

iii) for inhomogeneous states, both MF and PY theory generate far too high compressibility factors compared with computer data. However, while MF theory results deviate by 20–30 per cent from the exact value, PY theory gives much too high numbers.

iv) the compressibility factors generated by the MD and MC calculations remain constant in the two phase region. This is consistent with the picture of an unstable demixing state of the system. Such a behaviour can, of course, not be described by MF and PY approximations.

Table 4 Compressibility factor of the equimolar Widom–Rowlinson mixture calculated by molecular dynamics and Monte-Carlo methods as well as Percus–Yevick and mean field approximations.

state	n^*	$z^{\mathrm{MD}*)}$	z^{MC}	z^{PY}	z^{MF}
1	0.1785	1.192 ± 0.005	1.178 ± 0.003	1.181	1.187
2	0.2381	1.252	1.230	1.235	1.249
3	0.2976	1.298	1.279	1.286	1.312
4	0.3571	1.335	1.320	1.331	1.374
5	0.4166	1.385	1.347	1.372	1.436
6	0.4761	1.40 ± 0.01	1.37 ± 0.01	1.140	1.499
7	0.5356	1.40	1.38	1.448	1.561
8	0.5951	1.41	1.38	1.503	1.623
9	0.6546	1.40	1.38	1.626	1.686
10	0.7142	1.40	1.38	1.926	1.748
11	0.7737	1.39	1.39	2.880	1.810

*) Chosen temperature: $Tk/\varepsilon = 1 \pm 0.5$. The fat line separates homogeneous from inhomogeneous states.

Table 5 Compressibility factor of the WR model at mole fraction 0.75 (see Table 4 for details).

state	z^{MD}	z^{PY}	z^{MF}
1	1.148 ± 0.005	1.137	1.140
2	1.195	1.179	1.187
3	1.224	1.219	1.234
4	1.262	1.256	1.280
5	1.302	1.289	1.327
6	1.319	1.320	1.374
7	1.33 ± 0.01	1.348	1.420
8	1.34	1.376	1.467
9	1.34	1.410	1.514
10	1.33	1.466	1.561
11	1.35	1.592	1.608

We conclude that for the equimolar WR mixture, both MF and PY theory are well suited to describe the compressibility factors in a large region of states. For unstable, inhomogeneous states the PY approximation is inferior, which may be regarded as indication of the insufficiently predicted critical phase separation density by the PY approach.

For mole fraction 0.75, the comparison of compressibility factor calculated by the various methods can be made in Table 5. This table supports essentially the findings discussed for the equimolar mixture. Systematic Monte Carlo results have not been produced for this composition in view of the well agreeing data for the HS and the HSS mixture compared in Table 4.

3.3 Pair correlation function at contact

With regard to the results discussed in Sec. 3.2 it was interesting to compare the contact value of the radial pair correlation function calculated by PY as well as MD and MC methods. The contact value, g_{12}, of the pair correlation function for the HSS system cannot be evaluated very accurately due to the softness of this potential. The error bars indicated in Table 6 contain these uncertainties beside the numerical statistical uncertainty. The computer results for the HS and the HSS system agree well within the mutual error bars, however, with a slight tendency of the HSS g_{12} values to underestimate the contact value, as expected.

The PY g_{12} values are throughout smaller than the exact Monte Carlo results, although there is reasonable agreement for lower densities. For denser states, even the homogeneous ones, the PY approximation generates about 10–30 per cent too high contact values. At the highest density considered it gives an unreasonably large g_{12} value not included in the table.

Nevertheless overall agreement of exact and PY g_{12} values is acceptable, particularly with regard to the fact that the MF approximation assumes $g_{12} = 1$ for all the states.

Table 6 Contact values of the pair correlation function of unlike pairs of the equimolar Widom-Rowlinson model calculated by molecular dynamics and Monte-Carlo methods as well as the Percus-Yevick approximation (see Table 4 for details).

state	g_{12}^{MD}	g_{12}^{MC}	g_{12}^{PY}
1	0.96 ± 0.02	0.959 ± 0.005	0.968
2	0.91	0.920	0.944
3	0.88	0.890	0.917
4	0.85	0.855	0.885
5	0.80	0.795	0.853
6	0.72 ± 0.03	0.74 ± 0.01	0.822
7	0.65	0.68	0.799
8	0.59	0.61	0.807
9	0.55	0.54	0.913
10	0.53	0.51	1.286
11	0.46	0.49	

4 CONCLUDING REMARKS

We have demonstrated that the hard sphere potential and the 42 'hard soft sphere' potential give practically equivalent numerical results for the static quantities of the corresponding Widom–Rowlinson fluids. This is in agreement with previous findings for the dynamic behaviour of the HS and the HSS system at high densities and results for static quantities of the so called Bearman–Mazo model mixture[7]. Thus the 42-HSS model appears to be a very good approximation to the real HS system with the advantage of having a continuous potential function for the MD.

Our calculations showed furthermore that mean field and Percus–Yevick approximations are both very appropriate to predict the compressibility factors of the WR mixture in a large density region. For lower densities, the PY theory even generates exact results. In the two phase region MF and PY descriptions are equivalent aside from very dense states, where the MF approximation is preferable. This fact may explain why the critical phase separation density of the WR mixture is too high predicted by the PY theory.

The contact value of the pair correlation function g_{12} is reasonably predicted by the PY theory, although there appear significant deviations from the Monte Carlo results in the two-phase region.

Oppositely, the contact value of unity assumed by the MF theory is an overestimate for most states excepting those of very small density.

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