The influence of thermodynamic self-consistency on the phase behaviour of symmetric binary mixtures

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Abstract

We have investigated the phase behaviour of a symmetric binary mixture with particles interacting via hard-core Yukawa potentials. To calculate the thermodynamic properties we have used the mean spherical approximation (MSA), a conventional liquid state theory, and the closely related self-consistent Ornstein–Zernike approximation which is defined via an MSA-type closure relation, requiring, in addition, thermodynamic self-consistency between the compressibility and the energy-route. We investigate on a quantitative level the effect of the self-consistency requirement on the phase diagram and on the critical behaviour and confirm the existence of three archetypes of phase diagram, which originate from the competition between the first order liquid/vapour transition and the second order demixing transition.
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1. Introduction

Nowadays, the phase behaviour of simple one-component fluids can be determined with high accuracy by means of accurate and efficient liquid state methods [1–3]. Methodological and numerical sophistication has reached a level where classical liquid state methods (such as integral-equation approaches or perturbation theories) provide results that are indistinguishable from computer simulation data; this holds not only for 'standard' state points but also for the critical region and near phase boundaries. Thus, it is high time to extend this expertise to more-component systems. Indeed, considerable effort has been devoted in recent years to this field: meanwhile it has become possible to determine not only the phase diagram of selected binary mixtures ([4–10] and references quoted therein), but also that of ternary systems [11]; one should also point out that remarkable progress has been made in investigations of the phase behaviour of polydisperse fluid mixtures [12]. The concepts of liquid state theories for the multi-component case are straightforward methodological extensions of well-tested and well-functioning approaches developed for one-component systems; of course the step towards more-component systems is accompanied by an increasing computational effort. Nevertheless, optimized numerical algorithms (well-tested in the one-component case) along with an increase in computational power of present day workstations have made it possible to study the phase behaviour of selected multi-component systems not only on a qualitative but also on a quantitative level.

Still, the now considerably larger number of system parameters of two-component mixtures represents a major obstacle to the investigation of the phase behaviour of such systems in a *systematic* way. It is, therefore, not surprising that the only comprising study of the phase behaviour of binary mixtures, which is based on a van der Waals model, dates back to 1980 [13] and is nowadays still the only available systematic investigation in this field. Even though this study has—as a consequence of the simplicity of the van der Waals approach—rather a qualitative than a quantitative character, it offers a deeper insight into the phase behaviour of binary mixtures: for instance, all phase diagrams that can be encountered for such systems have been classified by archetypes. This paper serves as *the* reference article

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for investigations in this field. However, a systematic reinvestigation of two-component systems as it was done by van Konynenburg and Scott, but now on a *quantitative* level with the help of reliable liquid state methods would still today be out of reach of the available computational power. Being forced to find a compromise between feasibility and quantitative calculations, scientists have started their investigations by choosing special binary systems with a reduced number of system parameters.

In this sense, the most simple binary systems to be considered are symmetric mixtures: here the two pure components (labeled by '1' and '2') are identical while the interaction between dissimilar species differs. Thus, the interatomic potentials between the different species, $\Phi_{ij}(r)$, $(i,j=1,2)$ are fixed via the following relations $\Phi_{11}(r) = \Phi_{22}(r) = (1/\alpha)\Phi_{12}(r)$. For simplicity, we take hard-core Yukawa (HCY) interactions for the $\Phi_{ij}(r)$. Indeed, the system is now characterized—apart from the parameters that describe the $\Phi_{ij}(r)$ as such—by temperature, density, concentration, and α; in particular α will be identified as *the* relevant system parameter that is responsible for the classification of the phase diagrams in terms of archetypes. Several investigations were devoted in recent years to the study of the phase behaviour of such systems [4–10]. Despite the restricted number of parameters, the phase behaviour of these systems is nevertheless very interesting and rather complex: it is characterized by the competition between the (first order) liquid/vapour transition and the (second order) demixing transition. Depending on where the liquid/vapour coexistence curve intersects the λ-line (i.e. the line of critical points of the demixing transition), three archetypes of phase diagrams can be identified, which are characterized by critical phenomena such as critical end points and tricritical points. Although the occurrence of these three archetypes has meanwhile been commonly accepted, doubts have been raised lately regarding some issues: in a recent study the existence of one of the types of phase diagrams [9] was questioned and in another contribution a debate on the order of the demixing transition [7] was presented.

In the present contribution, we have used two liquid state methods to calculate the phase diagram of a symmetric binary mixture: the mean spherical approximation (MSA) [14] and the self-consistent Ornstein–Zernike approximation (SCOZA) ([2] and references therein). Both methods start from very similar closure relations: while the MSA is a conventional liquid state method that provides reasonably accurate data for structural and thermodynamic data, the SCOZA requires, in addition, a thermodynamic self-consistency between two thermodynamic routes. In contrast to the MSA, SCOZA can be solved even in critical regions and is capable of providing quantitatively correct results in these parts of the phase diagram (for an overview see Refs. [2,15]).

As noted above, we have used HCY interactions, a choice of which is justified by the fact that the MSA can be solved semi-analytically for a HCY mixture with an arbitrary number of components [16,17]; the SCOZA formalism, in turn, benefits of the availability of the MSA-solution for this system [8,15]. The aim of the paper is two-fold: first, we want to study on a quantitative level the effect of the self-consistency requirement on the phase behaviour; second, we want to contribute to the controversial question about the number of archetypes of phase diagrams to be expected for such a system.

The paper is organized as follows: in the subsequent section we present the system, briefly introduce the concepts of the two liquid state methods involved, and outline how the phase diagram was determined. In Section 3, we present and discuss our results. The paper is closed with concluding remarks.

2. Theory

2.1. The system

In our symmetric binary mixture, the particles interact via HCY potentials $\Phi_{ij}(r)$. The interaction between the like particles is the same $[\Phi_{11}(r) = \Phi_{22}(r)]$, while the interatomic potentials of unlike particles is given by $\Phi_{12}(r) = \alpha\Phi_{ii}(r)$. Thus, the repulsive hard-core (HC) is characterized for all three interactions, by a diameter σ

$$\Phi_{ij}(r) = \begin{cases} \infty & r \le \sigma \\ w_{ij}(r) & r > \sigma \end{cases} . \tag{1}$$

For the $w_{ij}(r)$, the attractive tails, we use Yukawa potentials, i.e.

$$w_{11}(r) = -\frac{1}{r}\exp[-z(r-1)]. \tag{2}$$

z is the screening length of the potential; the HC diameter σ and the interaction strength of the attractive tail, ε_{11}, have been set to unity. Further, the mixture is characterized by the temperature T $[\beta = (k_B T)^{-1}]$, the total number-density ρ, and the concentration $x = x_1$ of species 1; partial number densities are defined via $\rho_1 = x\rho$ and $\rho_2 = (1-x)\rho$. We further introduce the reduced dimensionless quantities, $\rho^\star = \rho\sigma^3$ and $T^\star = k_B T\sigma/\varepsilon_{11}$.

2.2. Liquid state theories

Both MSA and SCOZA are based on the Ornstein–Zernike relation (OZ) [14] which reads

$$h_{ij}(r) = c_{ij}(r) + \sum_k \rho_k \int d\mathbf{r}' c_{ik}(r')h_{kj}(|\mathbf{r}-\mathbf{r}'|), \quad i,j=1,2$$

$$\tag{3}$$

The $h_{ij}(r)$ and the $c_{ij}(r)$, $i,j=1,2$ are the total and the direct correlation functions, the $g_{ij}(r)=h_{ij}(r)+1$ are the pair distribution functions.

2.2.1. Mean spherical approximation

In the MSA, the OZ-equations are supplemented by the closure relation

$$g_{ij}(r)=0 \qquad \text{for } r\leq 1$$
$$c_{ij}(r)=-\beta w_{ij}(r) \quad \text{for } r>1. \tag{4}$$

Based on earlier work by Blum and Høye [16], Arrieta et al. [17] have presented a formalism which permits to solve the MSA for a HCY mixture with an arbitrary number of components and an arbitrary number of Yukawa tails (characterized by different screening lengths z_n). It leads to sets of coupled non-linear equations. From their solution, the structure functions and—via different thermodynamic routes—thermodynamic properties can be calculated. However, as a consequence of simplifying approximations that lead to the MSA closure relation Eq. (4), different thermodynamic routes (such as the virial-, the energy- or the compressibility-route) lead to different results for the thermodynamic properties; MSA is a thermodynamically inconsistent liquid state theory.

2.2.2. Self-consistent Ornstein–Zernike approximation

The SCOZA starts from a similar closure relation as Eq. (4), i.e.

$$g_{ij}(r)=0 \qquad\qquad \text{for } r\leq 1$$
$$c_{ij}(r)=c_{HC;ij}(r)+K_{ij}(\rho,T,x)w_{ij}(r) \quad \text{for } r>1. \tag{5}$$

The $c_{HC;ij}(r)$ are the direct correlation functions of the HC reference system: here we have used the Waisman parametrization for this function [18], i.e. $c_{HC}(r)=(K_0/r)\exp[-z_0(r-\sigma)]$, with $K_0(\rho)$ and $z_0(\rho)$ being well-known functions of ρ (see Appendix of [2]). The functions $K_{ij}(\rho,T,x)$ are still undetermined and are fixed by the requirement that the theory is thermodynamically self-consistent. For the three unknown functions we require three consistency relations. As outlined in detail in Ref. [15], a fully thermodynamically self-consistent solution of the SCOZA is far too complex from the numerical point of view. We have there resorted to an approximate assumption, which is motivated by symmetry arguments: due to the symmetry of the system

$$K_{11}(\rho,T,x)=K_{22}(\rho,T,1-x) \tag{6}$$

$$K_{12}(\rho,T,x)=K_{12}(\rho,T,1-x). \tag{7}$$

We reduce the number of unknown functions to one single function $K(\rho,T,x)$ that is symmetric with respect to x and that is related to the $K_{ij}(\rho,T,x)$ via

$$K(\rho,T,x)=K_{ij}(\rho,T,x). \tag{8}$$

For this unknown function, we now enforce thermodynamic consistency between the energy- and the compressibility-route; this is done as follows. In the binary case, the energy-route reads

$$u=2\pi\sum_{ij}\rho_i\rho_j\int\Phi_{ij}(r)g_{ij}(r)r^2\,dr, \tag{9}$$

where u is the excess (over ideal gas) internal energy per volume; note that $u=u(\rho,T,x)$.

The partial compressibility-routes establish a link between the chemical potentials μ_i and the Fourier transforms of the direct correlation functions (characterized by a tilde) via

$$\rho_1\frac{\partial\beta\mu_1}{\partial\rho_1}=1-\rho_1\tilde{c}_{11}(q=0)$$

$$\rho_2\frac{\partial\beta\mu_2}{\partial\rho_2}=1-\rho_2\tilde{c}_{22}(q=0)$$

$$\rho_1\frac{\partial\beta\mu_1}{\partial\rho_2}=-\rho_1\tilde{c}_{12}(q=0)$$

$$\rho_2\frac{\partial\beta\mu_2}{\partial\rho_1}=-\rho_2\tilde{c}_{12}(q=0). \tag{10}$$

If the μ_i and u stem from a unique Helmholtz free energy, then the partial consistency relations

$$\frac{\partial^2 u}{\partial\rho_i\partial\rho_j}=\frac{\partial}{\partial\beta}\left(\frac{\partial\beta\mu_j}{\partial\rho_i}\right) \quad i,j=1,2 \tag{11}$$

hold. Since we now have only one unknown function $K(\rho,T,x)$ we can use instead of the three partial consistency relations Eq. (11) only one relation which we obtain from a suitable linear combination of these relations, like, e.g.

$$\rho\frac{\partial^2 u}{\partial\rho^2}=\frac{\partial}{\partial\beta}\left(1-\frac{1}{\rho}\sum_{ij}\rho_i\rho_j\tilde{c}_{ij}(q=0)\right)=\frac{\partial}{\partial\beta}\left(\frac{1}{\chi_{red}}\right) \tag{12}$$

with the reduced dimensionless isothermal compressibility $\chi_{red}=\rho k_B T\chi_T$ given by

$$\chi_{red}=\left(\frac{\partial\beta P}{\partial\rho}\right)^{-1}. \tag{13}$$

χ_T is the isothermal compressibility.

We point out that the left hand side of the partial differential equation (PDE) Eq. (12) is calculated via the energy-route while the right hand side is determined via the compressibility-route, thus enforcing the consistency between these two thermodynamic routes. As a consequence of the above assumption, the concentration x has become a simple parameter: thus, the consistency PDE Eq. (12) can be solved for different x-values independently.

Taking benefit of the availability of the semi-analytical MSA solution for a HCY mixture, the SCOZA formalism transforms the consistency PDE Eq. (12) into a PDE for the internal energy $u = u(\rho,T,x) = u(\rho,T)$

$$B(\rho,u)\frac{\partial u}{\partial \beta} = C(\rho)\frac{\partial^2 u}{\partial \rho^2},\tag{14}$$

where $B(\rho,u)$ and $C(\rho)$ are functions for which explicit expressions can be provided; for details of the SCOZA formalism for this system we refer the reader to Refs. [8,15].

The SCOZA-PDE Eq. (14) is solved with an implicit finite difference algorithm with suitable boundary conditions at $\rho = 0$ and $\rho_0 = 1$ and a suitable initial condition at $\beta = 0$. Details of the numerical solution are summarized in Refs. [8,15]. Once $u(\rho,T,x)$ has been determined numerically, the relevant thermodynamic quantities required for the determination of phase coexistence (i.e. pressure P and chemical potentials μ_i) are obtained via standard thermodynamic routes (cf. equations (44)–(46) in Ref. [8]).

2.3. Coexistence conditions

Since the solution of the SCOZA for the present system has turned out to be very time-consuming we have restricted ourselves to the equimolar case (for the *full* phase diagram of the binary symmetric mixture see Ref. [9]). From the Gibbs' phase rule we expect up to four phases to be in equilibrium, i.e. the vapour (G), the mixed fluid (MF), and the two (symmetric) phases of the demixed fluid (DF). As a consequence of their symmetry, theses phases are often referred to in literature as one single phase.

The phase diagram is calculated by solving the coexistence equations, i.e. equal chemical potentials and equal pressure of the coexisting phases at a given temperature. We characterize the coexisting phases by (ρ,x) and (ρ',x') and proceed as follows: the G-MF coexistence curve is obtained by solving the set of equations

$$\mu_i(\rho,T,x=1/2) \equiv \mu(\rho,T,x=1/2)$$

$$= \mu(\rho',T,x=1/2)\tag{15}$$

$$P(\rho,T,x=1/2) = P(\rho',T,x=1/2).\tag{16}$$

For the G-MF and the MF-DF transitions we proceed in two steps: first we determine the phase diagram of the demixing transition, i.e. looking at a given temperature T for two coexisting states with the same fluid density but different composition by fixing $\rho = \rho'$ and by determining concentrations x and $x' = 1-x$ of the coexisting phases. The equilibrium condition for the pressure is automatically fulfilled, while the equilibrium conditions for the chemical potentials become at given T and ρ

$$\mu_1(\rho,T,x) = \mu_2(\rho,T,x)\tag{17}$$

which defines (if it exists) the line $x(\rho)$ of the second order demixing transition. Along this line, the chemical potentials of the two species are equal by construction; they are denoted by $\mu[T,\rho,x(\rho)]$. In second step, the solution of the two equations

$$\mu[\rho,T,x=1/2] = \mu[\rho',T,x(\rho')]\tag{18}$$

$$P[\rho,T,x=1/2] = P[\rho',T,x(\rho')]\tag{19}$$

gives the density ρ of the G or MF and the density ρ' of the DF with concentrations $x(\rho')$ and $1-x(\rho')$, in equilibrium.

3. Results

In Figs. 1 and 2, we show the phase diagrams for a symmetric binary HCY mixture for two values of screening length z, $z = 1.8$ (Fig. 1) and $z = 2.5$ (Fig. 2) and three different α-values as indicated; MSA and SCOZA have been used as liquid state methods. In the latter case, the coexistence equations were solved with a Newton–Raphson algorithm, implemented in a FORTRAN90-program. For the MSA, the coexistence conditions were solved with MATHEMATICA taking benefit of the availability of analytic expressions for the thermodynamic data; a particular advantage of this symbolic language is the possibility of a pre-defined numerical accuracy of the results, which, especially in critical regions, was found to be very useful. The SCOZA PDE Eq. (14) could be solved even in the critical region of the G-MF transition and very close to the tricritical point (see below). In the MSA, the situation is much more delicate: despite high accuracy requirements imposed, the solution algorithm breaks down in the vicinity of critical points. Gaps in the coexistence curves near critical points in Figs. 1 and 2 indicate the limits up to where the coexistence equations could be solved.

In agreement with the previous studies (and in contradiction to [9]) we could identify for both z-values

become identical. As the density is increased, the mixed fluid demixes at the λ-line.

ii. In the type III phase diagram ($\alpha=0.65$) the λ-line intersects the G-MF coexistence curve in its critical point, leading to a tricritical point (index 'tr'), where three phases (a gas, a 1-rich, and a 2-rich liquid) become critical at the same time; two order parameters (i.e. the density difference between the G and the MF and the concentration difference of the two DF phases) vanish simultaneously.

iii. In the type II phase diagram ($\alpha=0.70$), the λ-line intersects the G-MF slightly below its critical point.

Fig. 1. Phase diagram [projection onto the $(T^\star \rho^\star)$-plane] for a binary symmetric HCY mixture with screening length $z=1.8$ for different α-values as indicated. Full line – SCOZA, broken line – MSA. For a more detailed discussion of critical phenomena of the system see text or [8].
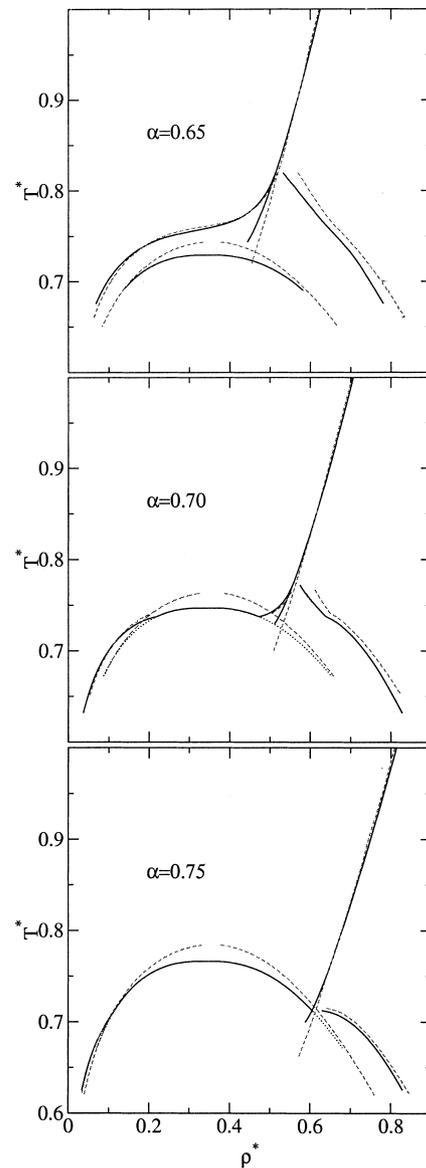
Fig. 2. Phase diagram [projection onto the $(T^\star \rho^\star)$-plane] for a binary symmetric HCY mixture with screening length $z=2.5$ for different α-values as indicated. Full line – SCOZA, broken line – MSA. For a more detailed discussion of critical phenomena of the system see text or [8].

and in qualitative agreement between the liquid state methods the three archetypes of phase diagrams (see also Ref. [5]):

i. In the type I phase diagram ($\alpha=0.75$) the λ-line approaches the G-MF coexistence well below the critical point; the intersection point is called a critical end point (CEP) where a critical liquid coexists with a non-critical gas. Below the CEP the gas, a 1-rich, and a 2-rich liquid coexist. Thus, the line below the CEP is a triple line. Above the CEP, the gas and the homogeneous liquid coexist up to the G-MF critical point. For higher temperatures, they

As in the preceding case we observe a tricritical point. Moreover, a triple point occurs where the G, the MF, and the DF (counted as a single phase) coexist.

Our results confirm the conclusions of previous computer simulations [10], mean field theories [5], and advanced liquid state methods [8,15] on the existence of three archetypes of phase diagrams of binary symmetrix liquid mixtures. The reasons why type I is not observed in the HRT study [9] is not clear. The authors have announced additional investigations, which will clarify this point. We can also state that a fourth type of phase diagram, where the λ-line ends at a CEP on the low density branch of the liquid/vapour coexistence line, could not be identified in our study; such a phase diagram was observed in a study on the phase behaviour of a Heisenberg fluid (see figure 12 in Ref. [19]), which—as other one-component systems with an additional degree of freedom—shows a phase behaviour similar to a symmetric binary mixture. We conclude that the existence of a type IV phase diagram should rather be questioned.

From Figs. 1 and 2, we learn that the agreement between the SCOZA and the MSA results for the phase diagrams is *qualitatively* very good. Of course, on the *quantitative* level differences are observed. For instance, the α-values where the phase diagrams change from one type to another will be slightly different in the two approaches. The most pronounced differences are observed for the liquid–vapour transition, in particular for the G-MF critical point: the MSA overestimates the critical temperature throughout, while the estimated value for the critical density fits nicely with the SCOZA-results. Larger discrepancies are also found for the tricritical point. The values obtained for T_{tr} and ρ_{tr} from the two liquid state approaches do not agree. Their difference seems more pronounced for the type II phase diagram. In contrast, for the CEP we find a much better coincidence of the data. An excellent agreement can also be observed for the λ-line. In all six systems investigated, the results obtained via SCOZA and MSA nearly coincide. The reason for this might be that the coexistence requirement Eq. (12) applies only to density but not to concentration. Thus, our SCOZA-results are not fully self-consistent, i.e. self-consistent both with respect to density *and* concentration. Complete self-consistency would be taken into account in the *full* SCOZA, introducing three unknown functions $K_{ij}(\rho,T,x)$ and using the three partial consistency relations Eq. (11). An additional requirement might lead to different results. In particular, it may cause a shift in the λ-line. However, such calculations are at present out of reach of computational power.

A final note is in order. One might argue that the HC reference system is not treated on equal footing in the MSA and the SCOZA. While the MSA reduces, for high temperatures, to the Percus–Yevick (PY) approximation for hard spheres, the SCOZA describes, in the same limit, the hard spheres in a self-consistent framework (Waisman parametrization), which might have an effect on the results. This question was discussed in a one-component study [2,20]. There it was shown that the different treatment of the HC reference system within the SCOZA leads only to minor changes in the critical temperature and density ($<2\%$). From these data, we can conclude that a simple PY treatment of the reference system in the SCOZA leads to a shift of the critical parameters away from the MSA results.

4. Conclusion

Determining the phase behaviour of an equimolar symmetric binary HCY mixture using the (conventional) MSA and the (thermodynamically self-consistent) SCOZA we were able to show how the self-consistency requirement effects the phase diagram on a *quantitative* level. Qualitative agreement is found to be very satisfactory. This concerns, in particular, the types of phase diagrams encountered. The largest differences are found for the location of the G-MF critical point and for the tricritical point. In both cases, MSA overestimates the respective critical temperatures. The density of the critical point is rather unaffected, while the density of the tricritical point is in the MSA larger than in the SCOZA. The agreement of the location of the CEP is very satisfactory and the λ-line coincides practically for both theories. This fact might be due to a restricted requirement in thermodynamic self-consistency in the present SCOZA version. Both MSA and SCOZA confirm the existence of three archetypes of phase diagrams, an issue that was debated recently in literature.

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