# Interfaces between two or three coexisting fluid phases in the system methane–perfluoromethane: Calculations with the Born-Green-Yvon equation[1]

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# Abstract

Wetting is studied for the binary mixture methane-perfluoromethane ($CH_4$–$CF_4$) with the Born-Green-Yvon equation in the Fischer-Methfessel approximation. The general phase behaviour is calculated with the consistent AMFA equation of state. Close to a three phase equilibrium $L_1L_2V$ perfect wetting of the interface $L_1V$ by the heavier liquid phase $L_2$ occurs. Liquid-vapour and liquid-liquid interfaces in the vincinity of the three phase equilibrium are calculated with the BGY equation and the surface tension is estimated from the density profiles. The results are compared to previous investigations of wetting in fluid systems, especially the theory of Cahn.



KEY WORDS: statistical mechanics; Born-Green-Yvon equation; liquid-vapour interfaces; wetting; surface tension; binary mixture; methane; perfluoromethane

# 1. Introduction

It was shown in a previous paper [1] that the Born-Green-Yvon (BGY) equation in the attractive mean field approximation (AMFA) by Fischer and Methfessel [2] is consistent with a van der Waals type equation of state, the AMFA equation of state, for both pure fluids and binary mixtures. Moreover, BGY results agree quite well with bulk phase equilibrium simulations with the NPT + test particle method for pure fluids and model mixtures and with liquid-vapour interface simulations for pure fluids and argon-krypton mixtures. In a second paper [3] the binary mixture methane–perfluoromethane ($CH_4$–$CF_4$) was studied with the BGY equation and the AMFA equation of state. Beside liquid-vapour interfaces also interfaces between two liquid or two liquid and a vapour phase were found. For liquid-vapour interfaces close to the liquid-liquid-vapour equilibrium wetting was observed. While increasing the bulk liquid concentration of $CH_4$ towards the value of the three phase equilibrium, a layer shows up in the interface and increases in thickness. Close to the three phase equilibrium this layer has a thickness of about 40 molecular diameters.

Wetting and wetting transitions have thoroughly been studied theoretically and experimentally. Wetting has been found at solid-gas interfaces by gradient theory theory (e.g. Teletzke et al. [4]), BGY equation (e.g. Wendland et al. [5]), density functional (DF) theory (e.g. Dhawan et al. [6]) and molecular simulation (e.g. Sokolowski et al. [7]), and at liquid-vapour interfaces by DF theory (e.g. Telo da Gama et al. [8]). Wetting has also been studied experimentally by Schmidt et al. [9] for liquid-vapour interfaces and by Taborek et al. [10] for solid-fluid interfaces. A survey of experimental and theoretical work on wetting phenomena is given by Franck [11] and Davis [12].

The agreement of the BGY results for the system $CH_4$–$CF_4$ with experimental and theoretical observations in the literature for different binary and ternary systems

needs to be discussed. Therefore, liquid-vapour and liquid-liquid interfaces in the vincinity of the three phase equilibrium, where wetting occurs, are more closely studied in the present paper. The surface tension, which is a measure if perfect wetting or non-wetting is observed, is calculated for the different types of interfaces and results are compared to the theories and observations of Cahn and Moldover [13, 14].

In section 2 of this paper the BGY equation and the numerical solution procedure are briefly reviewed. Section 3 gives the molecular model for the system $CH_4$–$CF_4$ and introduces the AMFA equation of state. In section 4 results of liquid-vapour and liquid-liquid interfaces in the system $CH_4$–$CF_4$ are discussed. Mainly the problem of wetting is addressed and results for the surface tension are given.

## 2. Outline of method

The BGY equation is used to calculate fluid-fluid interfaces of binary mixtures. Let us consider a mixture of two or more components with the intermolecular potentials $u_{\alpha\beta}(r)$ ($\alpha = a, b, \ldots$, $\beta = a, b, \ldots$). Statistical mechanics gives us expressions for the local densities $n_\alpha(\mathbf{r})$ of the components $\alpha$, which contain the integration over the Boltzmann-factors of all but one particle. Differentiation of $n_\alpha$ with respect to $\mathbf{r_1}$ yields one rigorous BGY equation for each component $\alpha$ [15, 16]

$$\nabla_{\mathbf{1}} \ln \rho_\alpha(\mathbf{r_1}) = -\sum_\beta \int \rho_\alpha(\mathbf{r_2}) g_{\alpha\beta}(\mathbf{r_1}, \mathbf{r_2}) \beta \nabla_{\mathbf{1}} u_{\alpha\beta}(r_{12}) d\mathbf{r_2} \qquad . \tag{1}$$

The approximation scheme by Fischer and Methfessel [2] in an extension to multicomponent mixtures [1, 15] is used. The intermolecular potentials $u_{\alpha\beta}$ are split into their repulsive and attractive parts according to the prescription of Weeks-Chandler-Andersen [17]. The pair correlation functions of the mean attractive forces are put equal to one. The softly repulsive potential is replaced by a hard sphere potential and the pair correlation function of the repulsive forces is approximated by the contact value of the pair correlation function $g^{\mathrm{H}}_{\alpha\beta,\mathrm{hom}}(r_{12} = d_{\alpha\beta}, ; \overline{\rho}_a, \overline{\rho}_b, \ldots)$

of a homogeneous hard sphere fluid at the coarse grained density $\overline{\rho}_\delta$ ($\delta = a, b, \ldots$). An expression for $g^{\mathrm{H}}_{\alpha\beta,\mathrm{hom}}(r_{12} = d_{\alpha\beta}, ; \overline{\rho}_a, \overline{\rho}_b, \ldots)$ derived by Boublík et al. [18] from Carnahan-Starling-Boublík-Mansoori equation [19, 20] is used. Details of the approximation scheme are given elsewhere [1, 3].

The density profiles of the components of a mixture at a liquid-vapour or liquid-liquid interface are the eigensolution of the BGY equation at a given temperature $T$ and a given bulk liquid concentration phase $x_\alpha$. The BGY equation is solved numerically by iteration. 40 grid points per molecular diameter ($d_{aa}$) are used for the numerical integration of the BGY equation, which is performed over a symmetric interval of 15 molecular diameters to each side of the Gibbs dividing surface. In some cases of liquid-vapour interfaces an asymmetric intervall with 15 molecular diameters on the gas side and up to 75 molecular diameters on the liquid side is used. Thus, the density profiles yield at their boundaries almost the orthobaric bulk densities and concentrations.

The surface tension of a multicomponent system can be calculated from the density profiles by (Ono and Kondo [21])

$$\beta\gamma = \frac{1}{4}\sum_\alpha\sum_\beta \int dz_1 \int d\mathbf{r_2}\rho_\alpha(\mathbf{r_1})\rho_\beta(\mathbf{r_2})g_{\alpha\beta}(\mathbf{r_1},\mathbf{r_2})\beta\frac{du_{\alpha\beta}(r_{12})}{dr_{12}}\frac{r_{12}^2 - 3z_{12}^2}{r_{12}} \quad , \tag{2}$$

if the pair correlation functions are approximated in the same way as in the BGY equation.

# 3. Molecular model and AMFA equation of state

The intermolecular forces are described by the Lennard-Jones (LJ) potential

$$u_{\alpha\beta}(r) = 4\varepsilon_{\alpha\beta}\left[\left(\frac{\sigma_{\alpha\beta}}{r}\right)^{12} - \left(\frac{\sigma_{\alpha\beta}}{r}\right)^{6}\right] \quad , \tag{3}$$

where the unlike interactions are calculated according to the combining rule

$$\varepsilon_{\alpha\beta} = \xi \sqrt{\varepsilon_{\alpha\alpha}\varepsilon_{\beta\beta}} \quad , \qquad \sigma_{\alpha\beta} = \frac{1}{2}\eta\left(\sigma_{\alpha\alpha} + \sigma_{\alpha\alpha}\right) \quad . \tag{4}$$

The LJ-parameters were already used elsewhere [3]:

$$\begin{aligned} &\sigma_{\mathrm{CF_4}} = 4.1910 \text{ Å} \quad , && \varepsilon_{\mathrm{CF_4}}/k = 203.68 \text{ K} \quad , \\ &\sigma_{\mathrm{CF_4}}/\sigma_{\mathrm{CH_4}} = 1.1 \quad , && \varepsilon_{\mathrm{CF_4}}/\varepsilon_{\mathrm{CH_4}} = 1.3586 \quad , \\ &\eta = 0.9054 \quad , && \xi = 1.0 \quad . \end{aligned} \tag{5}$$

For the numerical solution of the BGY equation the hard sphere diameters are set to $d_{\alpha\alpha} = \sigma_{\alpha\alpha}$. No cut-off is used for the LJ-potential. Hence, for this molecular model the bulk phase equilibria can be calculated from the AMFA equation of state:

$$A^{\mathrm{res}} = A^{\mathrm{res}}_{\mathrm{H}} + Nna \quad . \tag{6}$$

For the hard body part $A^{\mathrm{res}}_{\mathrm{H}}$ the Carnahan-Starling-Boublík-Mansoori equation [19, 20] is used and for the attractive energy part $Nna$ a van der Waals-type expression is derived from the model used in the attractive mean field approximation. The formuation of the AMFA equation of state is given elsewhere [1]. The AMFA equation of state is exact for the model, hard spheres plus attractive mean field approximation, which is used to approximate the BGY equation. Therefore it can be used to check the accuracy of the numerical solution of the BGY equation and to anticipate the bulk phase behaviour of the molecular model.

# 4. Results and discussion

In a previous paper [3] results for liquid-liquid ($L_1L_2$) and liquid-vapour ($L_1V$) interfaces of the system $CH_4(a)$–$CF_4(b)$ at 0.2 bar ($p\sigma^3_{aa}/\varepsilon_{aa} = 0.00145$) and 1.0133 bar ($p\sigma^3_{aa}/\varepsilon_{aa} = 0.00734$) calculated with the BGY equation and corresponding bulk phase equilibria with AMFA equation of state were presented. The results for the bulk phase properties with both methods were in a good to excellent agreement, as can also be seen from the isobaric temperature vs. concentration diagrams

in Fig. 1 and Fig. 2. At the higher pressure of 1 atm in Fig. 2 there is a simpler phase behaviour with a liquid-liquid equilibrium region at lower temperatures which ends in an upper critical solution temperature of about $kT/\varepsilon_{aa} = 0.791$ and a liquid-vapour region between $kT/\varepsilon_{aa} = 0.899$ and 1.22. At 0.2 bar, shown in Fig. 1, there is a more complicated phase behaviour with a liquid-vapour region, which is now found at lower temperatures, and a liquid-liquid region, which does not vary significantly with pressure. Both regions intersect at $kT/\varepsilon_{aa} = 0.75826$, which results in a three phase equilibrium $L_1L_2V$ between two liquids and a vapour and two types of liquid-vapour equilibria, $L_1V$ at temperatures above the three phase equilibrium and $L_2V$ at lower temperatures.

In the present paper results at 0.2 bar in the vincinity of the three phasee are more thoroughly studied. Fig. 3 gives density profiles of liquid-vapour interfaces of the type $L_1V$ for bulk liquid concentrations of $CH_4$(a) from $x_a = 0.01$ to 0.30. Only the profiles of the total density and the partial density of $CH_4$ are given. Results for the density profile of $CF_4$ are omitted to avoid confusion. At low $CH_4$ concentrations the total density decreases with slight oscillations from the bulk liquid to the bulk vapour density, while the partial density profile of $CH_4$ has – even at very low concentrations of $CH_4$ (e.g. $x_a = 0.01$) – a maximum in the interface. With increasing $x_a$ this maximum increases in height and thickness. At about $x_a = 0.20$ also a maximum in the total density shows up. With values of $x_a$ close to the AMFA results for the three phase equilibrium ($x_a = 0.343$) these maxima form a broad layer of constant density and concentration as can be seen from Fig. 4. The result at $x_a = 0.336$ (see also Fig. 5) is the closest to the three phase equilibrium we found with BGY equation. Here the layer has almost the same density and concentration as the second liquid phase $L_2$ in the three phase equilibrium. Results for the bulk phases and the layer with the BGY equation at $x_a = 0.336$ are compared in Table I to the AMFA equation of state results for the three phase equilibrium and agree well. Thus, the layer between the bulk phases $L_1$ and V is a thin layer of a third

wetting phase $L_2$. For a liquid-vapour interface near a liquid-liquid-vapour equilibria wetting can be expected. One of the two liquid phases, here $L_2$, is perfectly wetting the other liquid phase, $L_1$. In Fig. 5 also BGY results for the other two types of interfaces – $L_1L_2$ and $L_2V$ – which make up the three phase equilibrium are shown. The density profiles for $L_1L_2$ and $L_2V$ agree well with the result for $L_1V$, which is also confirmed by the bulk phase results in Table I.

The surface tension of the liquid-vapour interfaces for both isobars are compared in Fig. 6. Results for both isobars are similliar, but while the curve is continuous for 1 atm, there is a discontinuity at the temperature of the three phase equilibrium for 0.2 bar. The surface tension $\gamma_{L_1V}$ of the $L_1V$ interface decreases and the surface tension $\gamma_{L_2V}$ of the $L_2V$ interface increases while the three phase equilibrium is approached. Finally, when wetting occurs, the difference at the discontinuity is $\gamma_{L_1V} - \gamma_{L_2V} = 0.017$ (see Table I) which is equal to $\gamma_{L_1L_2} = 0.020$ within the uncertainty of the calculations. This result is in agreement to the theory of Cahn [13].

In case of equilibrium between three fluid phases or two fluid phases and a solid a generalization of Antonov's rule must be fulfilled. It can be written for the present case of two liquids – $L_1$ and $L_2$ – and a vapour V as:

$$\gamma_{L_1V} \leq \gamma_{L_1L_2} + \gamma_{L_2V} \quad . \tag{7}$$

Phase $L_2$ is not wetting the interface $L_1V$, as long as the inequality in equation (7) holds. In case of equality, phase $L_2$ will wet the $L_1V$ interface. Equation (7) can also be written as:

$$\gamma_{L_1V} - \gamma_{L_2V} \leq \gamma_{L_1L_2} \quad . \tag{8}$$

Cahn [13] argues that, if the critical point $L_1 = L_2$ is aproached, both, $\gamma_{L_1L_2}$ and $\gamma_{L_1V} - \gamma_{L_2V}$, will vanish as :

$$\begin{aligned} \gamma_{L_1L_2} &\propto (T_C - T)^{\mu} \\ \gamma_{L_1V} - \gamma_{L_2V} &\propto (T_C - T)^{\beta} \quad , \end{aligned} \tag{9}$$

where $\mu$ is about 1.3 and $\beta$ is in the range 0.3 to 0.4. As $\gamma_{L_1L_2}$ decreases faster than $\gamma_{L_1V} - \gamma_{L_2V}$, the inequality will become an equality at a temperature below the $L_1$ =$L_2$ critical temperature. Thus, perfect wetting of $L_2$ in the $L_1V$ interface does occur. This theory was later experimentally varyfied by Moldover and Cahn [14] for the system methanol–cyclohexane.

The present results are in an excellent agreement with the theory of Cahn. Phase $L_2$ is wetting the $L_1V$ interface at a temperature of $kT/\varepsilon_{aa} = 0.7583$ which is little below the critical temperature $kT_C/\varepsilon_{aa} = 0.791$. The results with the BGY equation for the surface tension between the different phases fulfill the equality in equation (9), as was already shown above.

# 5. Conclusion

The BGY equation in combination with the consistent AMFA equation of state has again been proven to be an interesting tool to investigate interfaces and wetting phenomena. In the system $CH_4$–$CF_4$ the formation of a perfectly wetting layer has been studied and is shown in three-dimensional plots. Furthermore, the surface tension, which is an important measure for the occurance of perfect or non-wetting, has been calculated. The results are in agreement with the theory of wetting by Cahn [13] and other theoretical and experimental investigations.

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Table I. Comparison of results for liquid-liquid and liquid-vapour interfaces for the LJ-mixture $CH_4(a)$-$CF_4(b)$ at $p\sigma_{aa}^3/\varepsilon_{aa} = 0.00145$ (0.2 bar) near the three phase equilibrium obtained from the BGY equation with results for the three phase phase equilibrium from the AMFA equation of state (EOS, $kT/\varepsilon_{aa} = 0.75826$).

| EOS | | | | BGY | | | | |
|---|---|---|---|---|---|---|---|---|
| type | phase | $x_a$ | $\rho\sigma_{aa}^3$ | type | phase | $x_a$ | $\rho\sigma_{aa}^3$ | $\gamma\sigma_{aa}^3/\varepsilon_{aa}$ |
| $L_1L_2V$ | $L_1$ | 0.34297 | 0.75400 | $L_1V$ | $L_1$ | 0.336 | 0.75331 | 1.149 |
| | $L_2$ | 0.74780 | 0.79458 | | layer | 0.7566 | 0.7955 | |
| | V | 0.97677 | 0.00194 | | V | 0.9779 | 0.00196 | |
| $L_1L_2V$ | $L_1$ | 0.34297 | 0.75400 | $L_1L_2$ | $L_1$ | 0.34297 | 0.75400 | 0.020 |
| | $L_2$ | 0.7478 | 0.79458 | | $L_2$ | 0.7652 | 0.7970 | |
| $L_1L_2V$ | $L_2$ | 0.74780 | 0.79458 | $L_2V$ | $L_2$ | 0.74780 | 0.79459 | 1.132 |
| | V | 0.97677 | 0.00194 | | V | 0.9778 | 0.00196 | |

# Figure captions

Fig. 1. Temperature vs. concentration diagram for the LJ-mixture $CH_4(a)$-$CF_4(b)$ at $p\sigma_{aa}^3/\varepsilon_{aa} = 0.00145$ (0.2 bar). BGY results ($L_1V$, $L_2V$: $\circ$; $L_1L_2$: $\diamond$) are compared with bulk phase equilibria from AMFA equation of state ($L_1V$, $L_2V$, $L_1L_2$: ———; $L_1L_2V$: – – –).

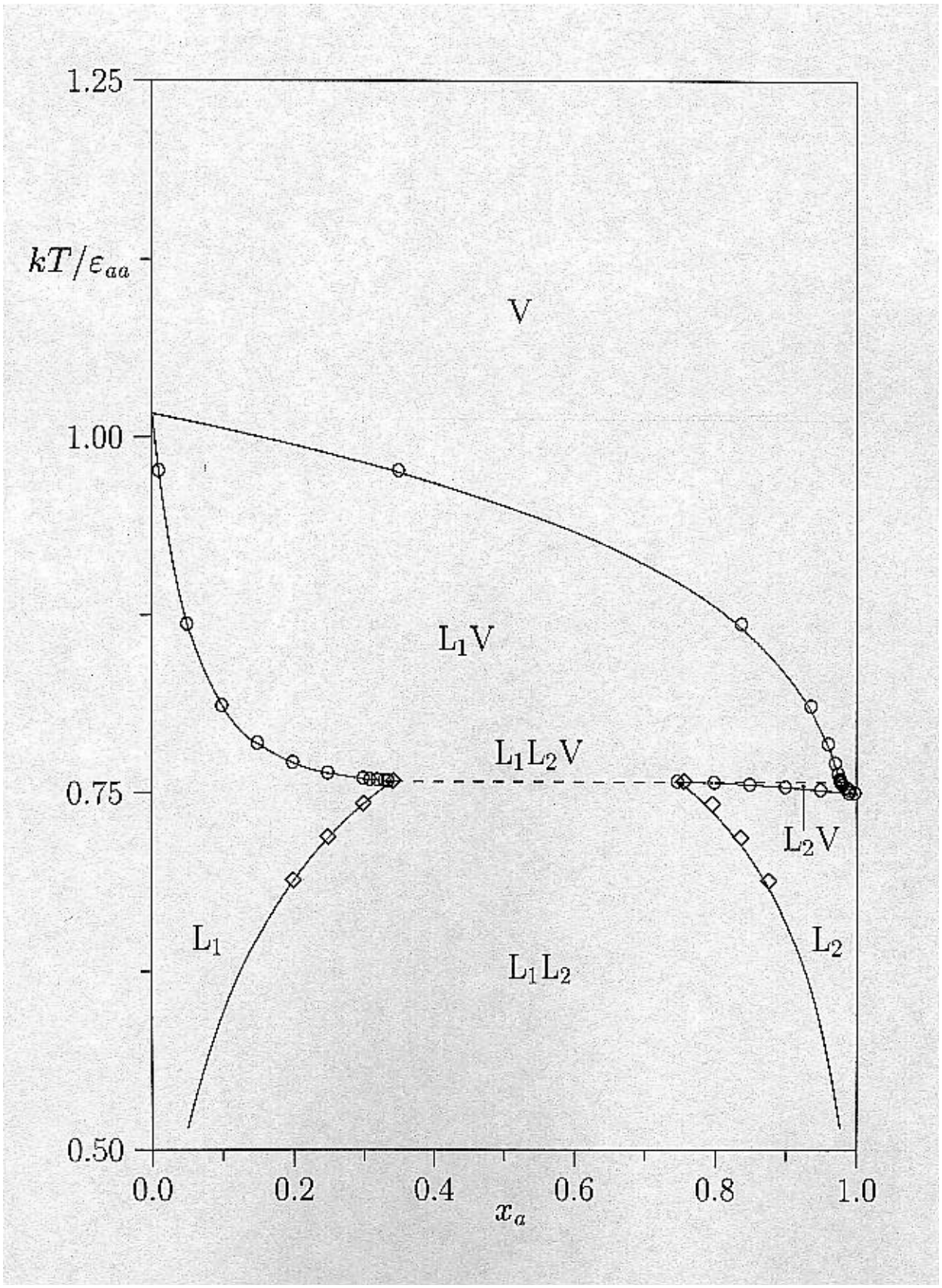
Fig. 2. Temperature vs. concentration diagram for the LJ-mixture $CH_4(a)$-$CF_4(b)$ at $p\sigma_{aa}^3/\varepsilon_{aa} = 0.00734$ (1 atm). BGY results (LV: $\circ$; $L_1L_2$: $\diamond$) are compared with bulk phase equilibria from AMFA equation of state (LV, $L_1L_2$: ———).

Fig. 3. Total (———) and $CH_4$ (– · – · –) density profiles of the liquid-vapour interface $L_1V$ for the LJ-mixture $CH_4(a)$-$CF_4(b)$ at $p\sigma_{aa}^3/\varepsilon_{aa} = 0.00145$ (0.2 bar) and at $CH_4$ concentrations between $x_a = 0.01$ and 0.30 obtained from the BGY equation.

Fig. 4. Total (———) and $CH_4$ (– · – · –) density profiles of the liquid-vapour interface $L_1V$ for the LJ-mixture $CH_4(a)$-$CF_4(b)$ at $p\sigma_{aa}^3/\varepsilon_{aa} = 0.00145$ (0.2 bar) and at $CH_4$ concentrations between $x_a = 0.30$ and 0.336 obtained from the BGY equation.

Fig. 5. Density profiles of liquid-liquid and liquid-vapour interfaces for the LJ-mixture $CH_4(a)$-$CF_4(b)$ at $p\sigma_{aa}^3/\varepsilon_{aa} = 0.00145$ (0.2 bar) near the three phase equilibrium obtained from the BGY equation.

Fig. 6. Surface tension vs. temperature diagram for the LJ-mixture $CH_4(a)$-$CF_4(b)$ at $p\sigma_{aa}^3/\varepsilon_{aa} = 0.00145$ (0.2 bar, $\circ$) and $p\sigma_{aa}^3/\varepsilon_{aa} = 0.00734$ (1 atm, $\diamond$) obtained from the BGY equation (The location of the three phase equilibrium is marked for convenience: – – –).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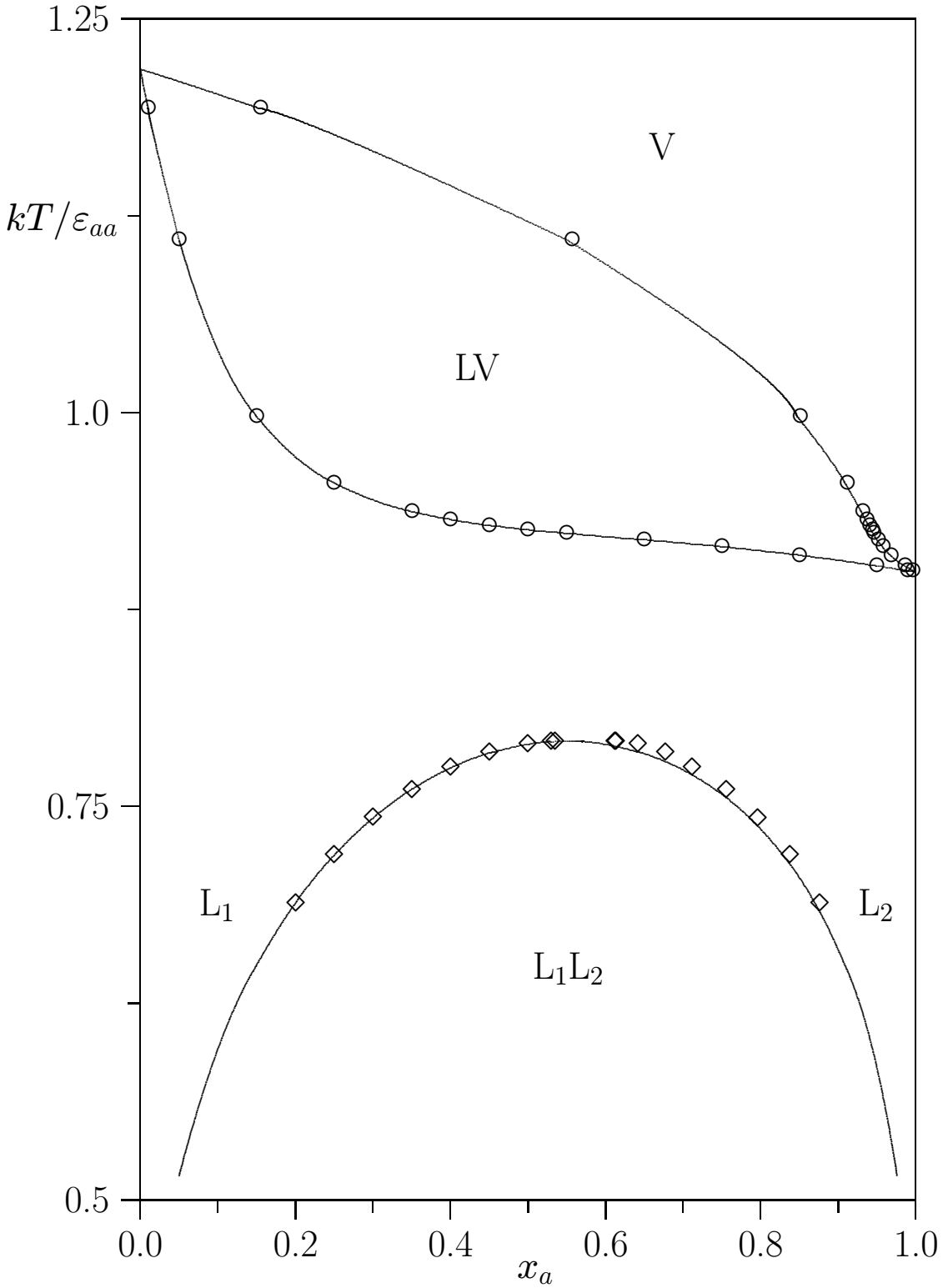
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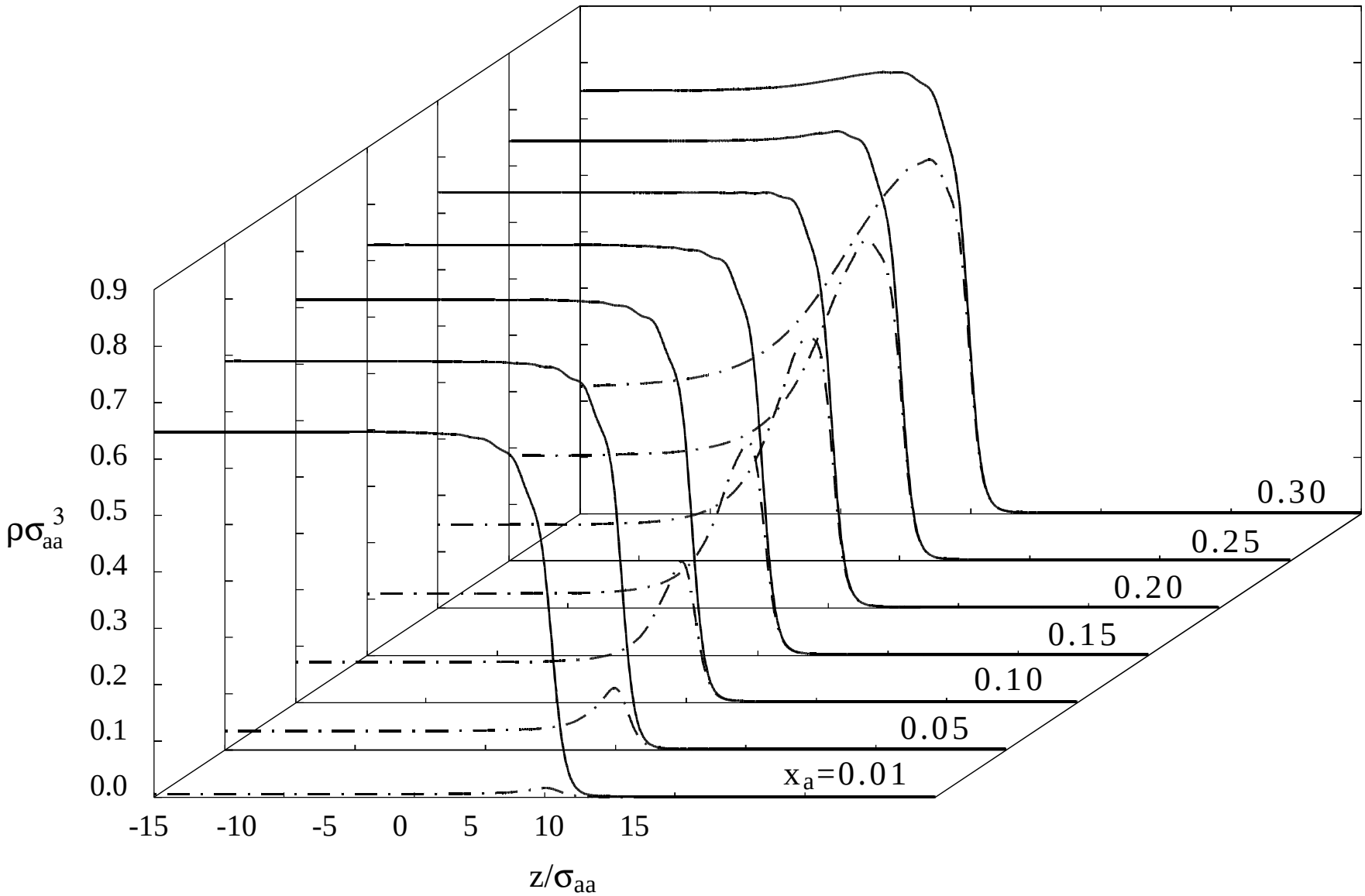
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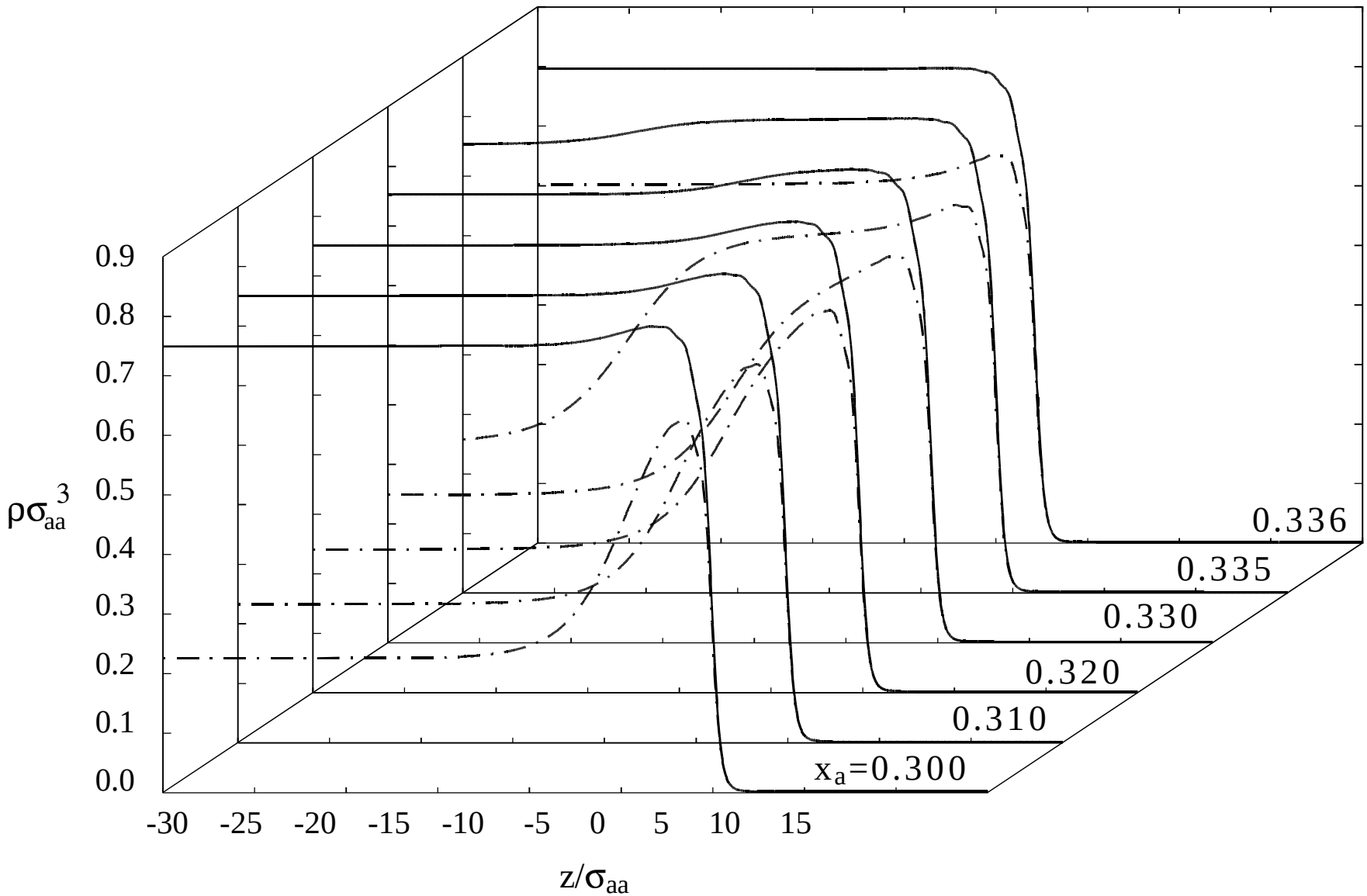
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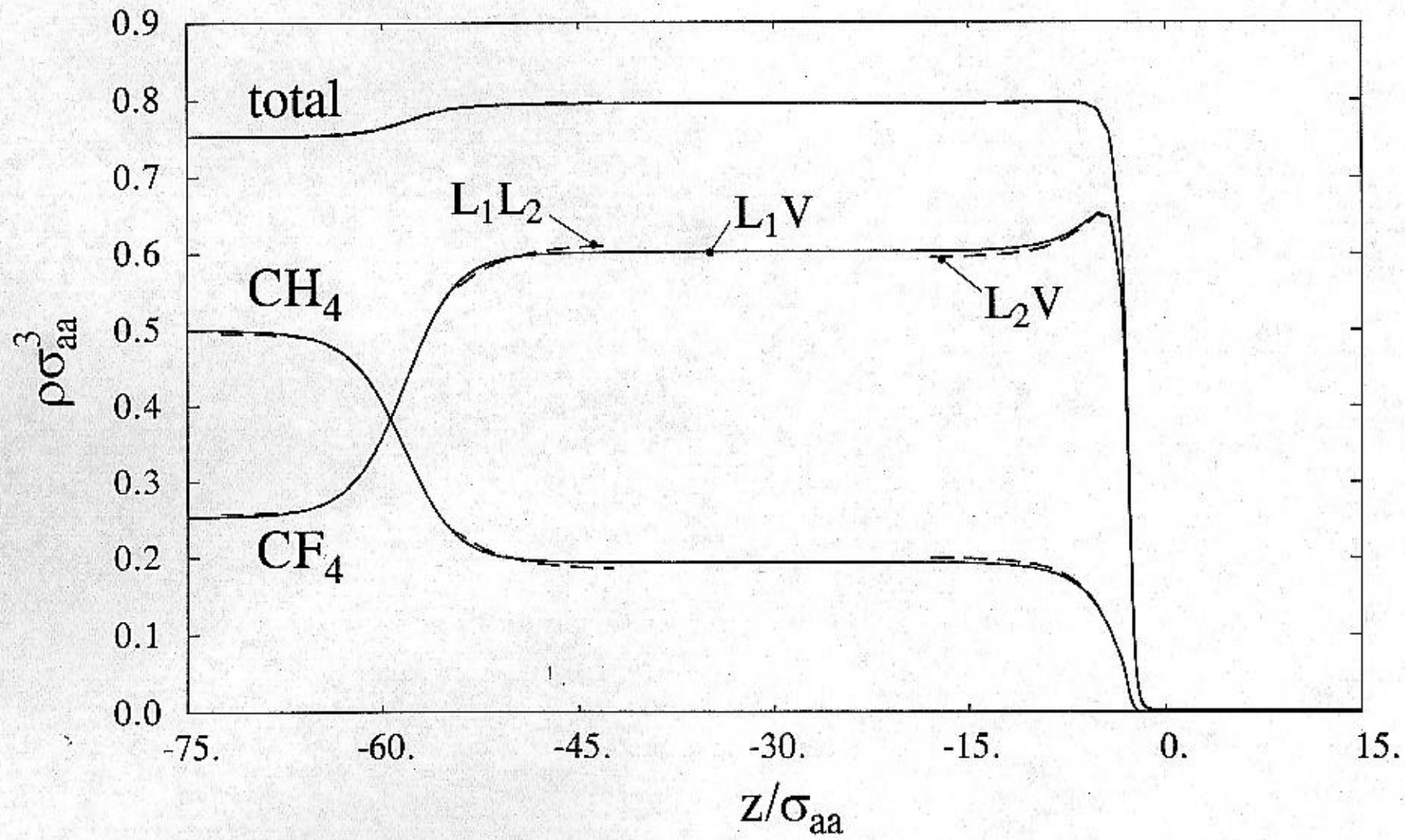
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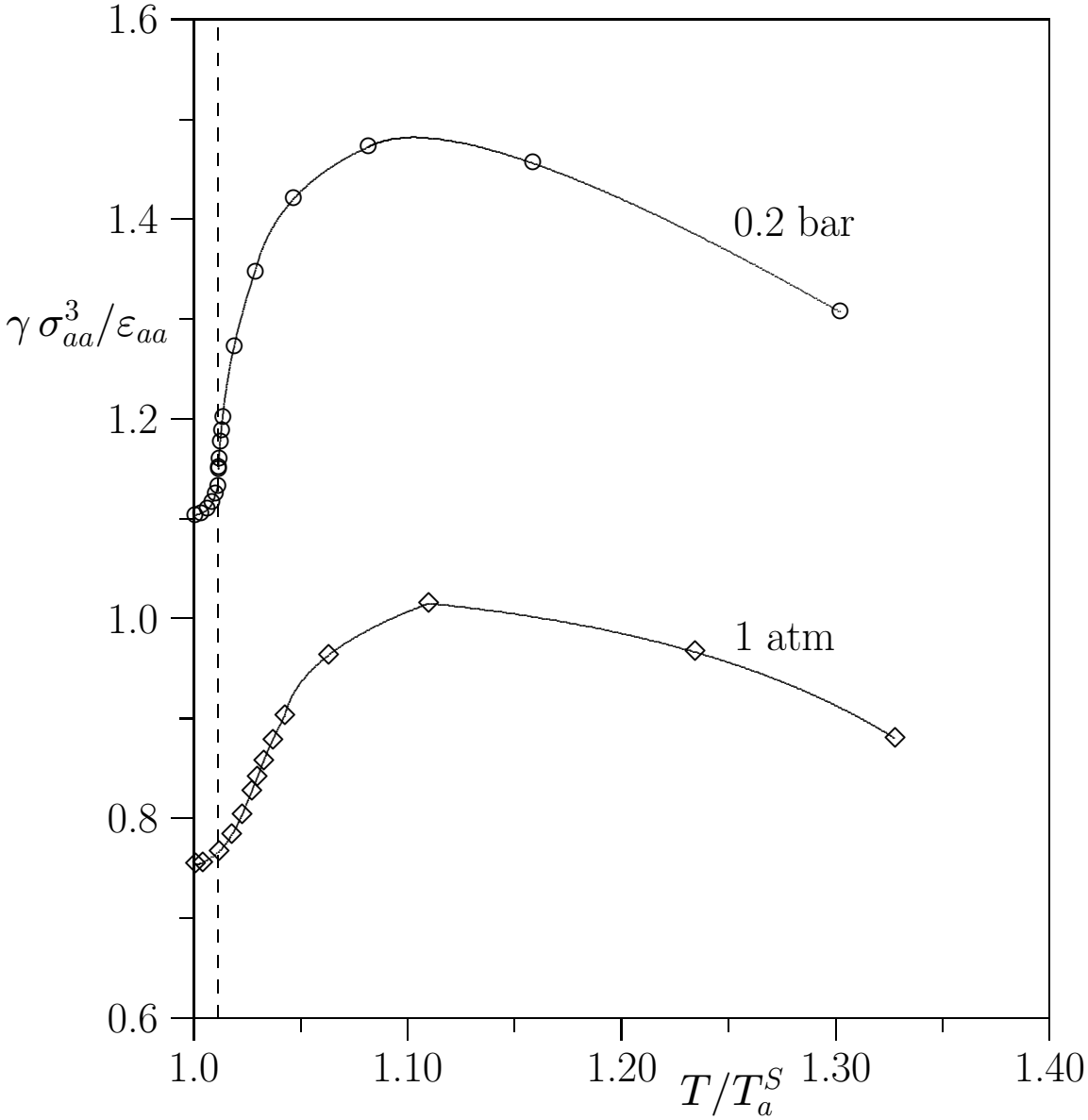
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1 atm
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1.40
$T/T_a^S$