Describing the properties of chains of segments interacting via soft-core potentials of variable range with the SAFT-VR approach

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Abstract

We present a general development for the equation of state of chain molecules composed of tangent spherical segments interacting with a soft repulsive potential and an attractive well. The method is based on a recent version of the statistical associating fluid theory for chain molecules with interaction potentials of variable range (SAFT-VR). In this communication we focus our attention on the properties of Lennard-Jones chains (LJC), using SAFT-VR and a simple recipe for the evaluation of the chain free energy that requires only a knowledge of the contact value of the cavity function of a Sutherland-6 system. We study the liquid-vapour coexistence properties for different values of the chain length. The results obtained are of similar accuracy to other EOS for LJC, but our approach is simpler and more general. We show that standard perturbation theories developed for simple liquids can also be used for chain molecules.

1 Introduction

The statistical associating fluid theory (SAFT) [1, 2] is a very accurate theory for the properties of a wide range of fluid systems and their mixtures. It is based on a perturbation theory for associating fluids proposed by Wertheim [3]-[8], where molecules are modelled as chains of spheres with dispersion forces, and short-range attractions that mimic association. The two major advantages of the SAFT approach are: that the equation of state is obtained from the properties of the constituent monomeric segments, and that each one of the terms can be directly compared with, and tested against, molecular simulation.

Several extensions of SAFT have been developed, differing from the original theory in the way that the monomer segments and the interactions are described. Complex association processes (e.g., the formation of ring aggregates [9]-[12], double bonding [13] and bond co-operativity [14]), as well as chains composed of dimer segments [15, 16] have been studied. The different versions of SAFT have all proven to be very successful in their description of real substances.

Recently, we have proposed a version of SAFT for hard spheres interacting via attractive wells of variable range (SAFT-VR) [17]. We have shown that the range parameter is a useful quantity in the description of experimental systems since it accounts for the non-conformal behaviour present in liquids and their mixtures. Moreover, SAFT-VR comprises a compact representation of the monomer properties, in the framework of the Barker and Henderson perturbation theory for simple liquids [18, 19, 20], which can be easily extended to mixtures.

In this paper we consider a further extension of SAFT-VR to account for chain molecules which are formed from soft-core segments with variable repulsive and attractive ranges. We demonstrate that the analytical expressions developed previously for the hard-core models together with a Barker and Henderson effective hard-sphere diameter [20] can be used for this purpose. As a specific application, we present an equation of state for Lennard-Jones chains. This system has been studied extensively in the past, and a number of accurate equations of state have been reported [21]-[25]. Our main goal is to show that SAFT-VR provides a simple and compact equation of state for LJC which is valid for ranges of density and temperature of practical interest.

We first summarise the SAFT-VR equation of state for hard-core systems interacting with a Sutherland-λ potential, and then use this model for a description of the Mie $m-n$ family of potentials [26], of which the Lennard-Jones potential is a specific case ($m = 6$ and

$n = 12$). We also present a simple recipe for the calculation of the free energy due to chain formation, and the prediction of LJC properties are compared with simulation results.

2 SAFT-VR for Pure Fluids

The Helmholtz free energy for associating chain molecules is described in the SAFT approach as

$$\frac{A}{NkT} = \frac{A^{IDEAL}}{NkT} + \frac{A^{MONO.}}{NkT} + \frac{A^{CHAIN}}{NkT} + \frac{A^{ASSOC.}}{NkT}, \tag{1}$$

where the different terms in this equation correspond to the contributions to the free energy due to the ideal fluid, the monomer segments, chain formation and intermolecular association, respectively.

The free energy of an ideal gas is given by [27]

$$\frac{A^{IDEAL}}{NkT} = \ln(\rho\Lambda^3) - 1, \tag{2}$$

where $\rho = N/V$ is the number density of chain molecules and not of monomer segments. Considering this term separately means that all of the other terms are residual free energies.

We consider that the general form of the monomer-monomer interaction is given by a hard-sphere repulsive term plus an attractive well:

$$u^M(r;\sigma,\epsilon,\lambda) = \begin{cases} \infty & \text{if } r < \sigma \\ -\epsilon\phi(r;\lambda) & \text{if } r > \sigma, \end{cases} \tag{3}$$

where σ is the spherical hard-core diameter, while ϵ, ϕ and λ are, the depth, the shape and the range parameter of the attractive well, respectively. In the SAFT-VR approach [17] different potential models can be used for the attractive well. Here, we will only consider the Sutherland potential, which takes the form,

$$\phi^S(r;\lambda) = (\sigma/r)^\lambda. \tag{4}$$

The range parameter λ controls the decay of the interaction. By varying λ, different angle-averaged multipolar-like forces, such as the Mie m-n potentials can be modelled with this potential.

The contribution to the free energy due to the monomers (m of which make up each chain molecule) interacting with a potential of the form given in Eq. (3) is

$$\begin{aligned} \frac{A^{MONO.}}{NkT} &= m_s \frac{A^M}{N_s kT} \\ &= m_s a^M, \end{aligned} \tag{5}$$

where N_s is the total number of spherical monomers, and $a^M = A^M/(N_s kT)$ is the excess Helmholtz free energy per monomer segment. An accurate description of a^M is obtained from the high-temperature expansion given by the Barker and Henderson perturbation theory for hard-core systems [18, 19, 20],

$$a^M = a^{HS} + \beta a_1 + \beta^2 a_2, \tag{6}$$

where $\beta = 1/kT$, and a_1 and a_2 are the first two perturbation terms associated with the attractive well. The mean-attractive energy a_1 is given by [20]

$$a_1 = -2\pi\rho_s\epsilon \int_\sigma^\infty r^2 \phi(r) g^{HS}(r)\, dr, \tag{7}$$

where $\rho_s = N_s/V$ is the density of monomers (segments) and $g^{HS}(r)$ is the radial distribution function of the hard-sphere reference system. By using the mean-value theorem, $g^{HS}(r)$ can be factorised from the integral and written in terms of its contact value $g^{HS}(1;\eta_{eff})$, an effective packing fraction η_{eff}, and the van der Waals mean-field term a_1^{VDW} [17]:

$$a_1 = a_1^{VDW} g^{HS}(1;\eta_{eff}), \tag{8}$$

where

$$g^{HS}(1;\eta_{eff}) = \frac{1-\eta_{eff}/2}{(1-\eta_{eff})^3}, \tag{9}$$

is obtained from the Carnahan and Starling expression [28]. In the case of the Sutherland potential,

$$a_1^{VDW} = -4\eta\epsilon \left(\frac{3}{\lambda - 3}\right), \tag{10}$$

where $\eta = \pi\sigma^3\rho_s/6$ is the packing fraction of the system, and

$$\eta_{eff}(\eta, \lambda) = c_1\eta + c_2\eta^2, \tag{11}$$

with

$$\begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} -0.943973 & 0.422543 & -0.0371763 & 0.00116901 \\ 0.370942 & -0.173333 & 0.0175599 & -0.000572729 \end{pmatrix} \begin{pmatrix} 1 \\ \lambda \\ \lambda^2 \\ \lambda^3 \end{pmatrix}. \tag{12}$$

The second-order term can be calculated in the local compressibility approximation [20],

$$a_2^S(\lambda) = \frac{1}{2}\epsilon K^{HS}\eta\frac{\partial a_1^S(2\lambda)}{\partial\eta}, \tag{13}$$

where K^{HS} is the Percus-Yevick hard-sphere isothermal compressibility, [20]

$$K^{HS} = \frac{(1-\eta)^4}{1+4\eta+4\eta^2}. \tag{14}$$

The contribution to the free energy due to the formation of a chain of m monomers is [1, 21]

$$\frac{A^{CHAIN}}{NkT} = -(m_s - 1)\ln y^M(\sigma), \tag{15}$$

where $y^M(\sigma)$ is the monomer-monomer background correlation function evaluated at hard-core contact; if $g^M(r)$ is the monomer-monomer radial distribution function, then $y^M(r) = \exp[u^M(r)/kT]g^M(r)$. In the SAFT-VR approach a perturbation expansion is used for the monomer-monomer contact value of the radial distribution function [20],

$$g^M(\sigma^+) = g^{HS}(\sigma^+) + \beta\epsilon g_1(\sigma^+), \tag{16}$$

and $g_1(\sigma^+)$ is obtained from a self-consistent calculation of the pressure, using the virial theorem of Clausius and the derivative of the free energy with respect to density. For the Sutherland potential we obtain [17]:

$$g^S(\sigma^+) = g^{HS}(\sigma) + \frac{1}{4}\beta\left[\frac{\partial a_1^S}{\partial\eta} - \frac{\lambda}{3\eta}a_1^S\right]. \tag{17}$$

The value of $g^S(\sigma^+)$ is also required in the calculation of the association free energy term. It must be stressed that all that is needed for the calculation of the complete equation of

state is a hard-sphere equation of state and the mean attractive energy a_1, which is given in terms of the hard-sphere contact value of g.

The contribution to the Helmholtz free energy due to association for s sites on the chain molecules is obtained from the theory of Wertheim as [29]

$$\frac{A^{ASSOC.}}{NkT} = \left[\sum_{a=1}^{s}\left(\ln X_a - \frac{X_a}{2}\right) + \frac{s}{2}\right], \tag{18}$$

where the sum is over all s sites a on a molecule, and X_a is the fraction of molecules not bonded at site a. The latter quantity is obtained by a solution of the following mass action equation:

$$X_a = \frac{1}{1 + \sum_{b=1}^{s} \rho X_b \Delta_{a,b}}. \tag{19}$$

The function $\Delta_{a,b}$ characterises the association between site a and site b on different molecules. It can be written in terms of the contact value $g^M(\sigma)$ of the monomer-monomer radial distribution function, the Mayer function $f_{a,b} = \exp(-\psi_{a,b}/kT) - 1$ of the a-b site-site bonding interaction $\psi_{a,b}$, and the volume $K_{a,b}$ available for bonding as [30]

$$\Delta_{a,b} = K_{a,b} f_{a,b} g^M(\sigma). \tag{20}$$

The bonding volume $K_{a,b}$ can be determined from the parameters of the bonding site such as its position and range [30]. As for the chain contribution, $g^M(\sigma)$ is approximated by $g^S(\sigma^+)$.

3 SAFT-VR for Lennard-Jones Chains

The expressions presented in the previous section can be used to develop an equation of state for chain molecules interacting via the Mie $m-n$ potentials [26], of which the Lennard-Jones ($m = 6$ and $n = 12$) is the most common example. The Mie $m - n$ potentials are given by

$$u^M = \mathcal{C}\epsilon\left[\left(\frac{\sigma}{r}\right)^n - \left(\frac{\sigma}{r}\right)^m\right], \tag{21}$$

where

$$\mathcal{C} = \frac{n}{n-m}\left(\frac{n}{m}\right)^{\frac{m}{n-m}}. \tag{22}$$

Systems interacting with binary potentials with soft repulsive interactions like Eq. (21) can be described within the Barker and Henderson perturbation theory, by considering an equivalent potential with a hard-core temperature dependent diameter,

$$u_{BH}^{M} = \begin{cases} \infty & \text{if } r < \sigma_{BH}(T) \\ u^{M} & \text{if } r > \sigma_{BH}(T), \end{cases} \tag{23}$$

where

$$\sigma_{BH}(T) = \int_0^{\sigma} (1 - \exp(-\beta u^{M}))dr, \tag{24}$$

and σ defines the position where u^M changes sign. The free energy is then calculated with the expansion (6) using the packing fraction

$$\eta_{BH}(T) = \eta \left(\sigma_{BH}/\sigma\right)^3 . \tag{25}$$

The expressions for a_1, a_2 and $g(\sigma^+)$ derived earlier (Eqs. (8), (13) and (17)) can be used directly in the expressions for the soft-core systems. Since the family of Mie potentials can be represented by a sum of an attractive and of a repulsive Sutherland potential, the mean-attractive energy for such systems can be expressed as the sum of two Sutherland a_1 terms,

$$a_1^{MIE} = \mathcal{C}\left[-a_1^S(\eta_{BH}; \lambda = n) + a_1^S(\eta_{BH}; \lambda = m)\right], \tag{26}$$

where a_1^S corresponds to the mean-attractive energy for a Sutherland system with exponent λ. The second order term a_2 is given in terms of the repulsive contribution only as

$$a_2^{MIE} = \mathcal{C} a_2^S(\eta_{BH}; \lambda = m). \tag{27}$$

For the LJ fluid we can apply this recipe with the following parametrisation for σ_{BH} [17]:

$$\sigma_{BH}/\sigma = 0.995438 - 0.0259917T^* + 0.00392254T^{*2} - 0.000289398T^{*3}, \tag{28}$$

where $T^* = kT/\epsilon$. In order to calculate the contribution to the free energy due to chain formation, we require the monomer cavity function at the bonding distance, y_b^M. For systems interacting with soft repulsive interactions, the bond distance is σ, i.e., where the potential is zero. Since in the SAFT-VR approach the molecules are formed from effective

hard-core segments with diameter σ_{BH}, the bond length is σ_{BH} and y_b^M can be calculated according to

$$y_b^M = y^{LJ}(\sigma_{BH}), \tag{29}$$

where y^{LJ} is the cavity function of the hard-core LJ potential from the Barker and Henderson perturbation theory. We have found that a more accurate prediction of the properties of the Lennard-Jones chains is obtained with the approximation

$$y_b^M = y^{S6}(\sigma_{BH}) \tag{30}$$

where y^{S6} is the Sutherland-6 potential contact value, obtained directly from Eq. (17). With this approximation, the final expression for the chain free energy is

$$\frac{A^{CHAIN}}{NkT} = -(m_s - 1) \ln y^{S6}(\sigma_{BH}). \tag{31}$$

4 Results

The vapour-liquid phase equilibria of Lennard-Jones chains of length m_s =2, 4 and 8 obtained using the SAFT-VR approach outlined in the previous section are compared with existing Gibbs ensemble Monte Carlo (GEMC) simulation results [25] in Figure 1. The SAFT-VR description for monomers ($m_s = 1$) given previously [17] and the corresponding GEMC simulation results [31] are also shown. The SAFT-VR theory gives a good overall description of the coexistence region, and reproduces the effect of increasing the chain length The theory's adequacy is, however, seen to decrease as the chain length increases, which can be rationalised in terms of an inaccurate description of molecular structure, such as folding, which occurs as the chain length increases [24]. It is well known that the SAFT approach accurately describes the behaviour of long-chain molecules up to $m_s = 8$ [15]. Various super-critical isotherms calculated using the SAFT-VR approach for LJC with m_s =2, 4 and 8 are presented in Figures 2, 3 and 4, respectively. The SAFT-VR expressions are seen to compare favourably with results obtained with the equation of state proposed by Johnson *et al.* [24]; these authors used an accurate empirical representation for $g^{LJ}(\sigma)$. The approximation used in Eq. (31) gives an accurate prediction of the vapour-liquid envelope, as well as the pressure for the whole range of monomer densities ρ_s^*. Our equation of state overpredicts the residual internal energy for densities $\rho_s^* > 0.7$.

5 Conclusions

We have presented a general equation of state for associating chain molecules interacting via potentials with soft-core repulsive interactions. This EOS is based on the recently developed SAFT-VR approach, together with a simple recipe for the evaluation of the chain free energy from the properties of the Sutherland-λ potential. We have seen that in the case of Lennard-Jones chains, an accurate description is obtained for vapour-liquid coexistence properties.

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References

[1] W. G. Chapman, K. E. Gubbins, G. Jackson, and M. Radosz, *Fluid Phase Equilibria*, **52**: 31 (1989); W. G. Chapman, K. E. Gubbins, G. Jackson, and M. Radosz, *Ind. Eng. Chem. Res.*, **29**: 1709 (1990).

[2] S. H. Huang and M. Radosz, *Ind. Eng. Chem. Res.*, **29**: 2284 (1990); S. H. Huang and M. Radosz, *Ind. Eng. Chem. Res.*, **30**: 1994 (1991).

[3] M. S. Wertheim, *J. Stat. Phys.*, **35**, 19 (1984).

[4] M. S. Wertheim, *J. Stat. Phys.*, **35**: 35 (1984).

[5] M. S. Wertheim, *J. Stat. Phys.*, **42**: 459 (1986).

[6] M. S. Wertheim, *J. Stat. Phys.*, **42**: 477 (1986).

[7] M. S. Wertheim, J̃. Chem. Phys., **85**: 2929 (1986).

[8] M. S. Wertheim, *J. Chem. Phys.*, **87**: 7323 (1987).

[9] D. Ghonasgi, V. Perez, and W. G. Chapman, *J. Chem. Phys.*, **101**: 6880 (1994).

[10] D. Ghonasgi and W. G. Chapman, *J. Chem. Phys.*, **102**: 2585 (1995).

[11] R. P. Sear and G. Jackson, *Phys. Rev. E*, **50**: 386 (1994).

[12] R. P. Sear and G. Jackson, *Mol. Phys.*, **87**: 517 (1996).

[13] R. P. Sear and G. Jackson, *Mol. Phys.*, **82**: 1033 (1994).

[14] R. P. Sear and G. Jackson, *J. Chem. Phys.*, **105**: 1113 (1996).

[15] D. Ghonasgi and W. G. Chapman, *J. Chem. Phys.*, **100**: 6633 (1994).

[16] F. W. Tavares, J. Chang, and S. I. Sandler, *Mol. Phys.*, **86**: 1451 (1995).

[17] A. Gil-Villegas, A. Galindo, P. J. Whitehead, S. J. Mills, G. Jackson, A. N. Burgess, *J. Chem. Phys.*, **106**: 4168 (1997).

[18] J. A. Barker and D. Henderson, *J. Chem. Phys.*, **47**: 2856 (1967).

[19] J. A. Barker and D. Henderson, *J. Chem. Phys.*, **47**: 4714 (1967).

[20] J. A. Barker and D. Henderson, *Rev. Mod. Phys.*, **48**: 587 (1975).

[21] W. G. Chapman, *J. Chem. Phys.*, **93**: 4299 (1990).

[22] D. Ghonasgi and W. G. Chapman, *Mol. Phys.*, **79**: 291 (1993).

[23] M. Banaszak, Y. C. Chiew, R. Olenick, and M. Radosz, *J. Chem. Phys.*, **100**: 3803 (1994).

[24] J. K. Johnson, E. A. Müller, and K. E. Gubbins, *J. Phys. Chem.*, **98**: 6413 (1994).

[25] F. A. Escobedo and J. J. de Pablo, *Mol. Phys*, **87**: 347 (1996).

[26] T. M. Reed and K. E. Gubbins, *Applied Statistical Mechanics*, (McGraw-Hill, Tokyo 1973).

[27] L. L. Lee, *Molecular Thermodynamics of Nonideal Fluids*, (Butterworth Publishers, Boston USA, 1988).

[28] N. F. Carnahan and K. E. Starling, *J. Chem. Phys.*, **51**: 635 (1969).

[29] W. G. Chapman, G. Jackson, and K. E. Gubbins, *Mol. Phys*, **65**: 1057 (1988).

[30] G. Jackson, W. G. Chapman, and K. E. Gubbins, *Mol. Phys.*, **65**: 1 (1988).

[31] A. Z. Panagiotopoulos, *Mol. Phys.*, **61**: 813 (1987).

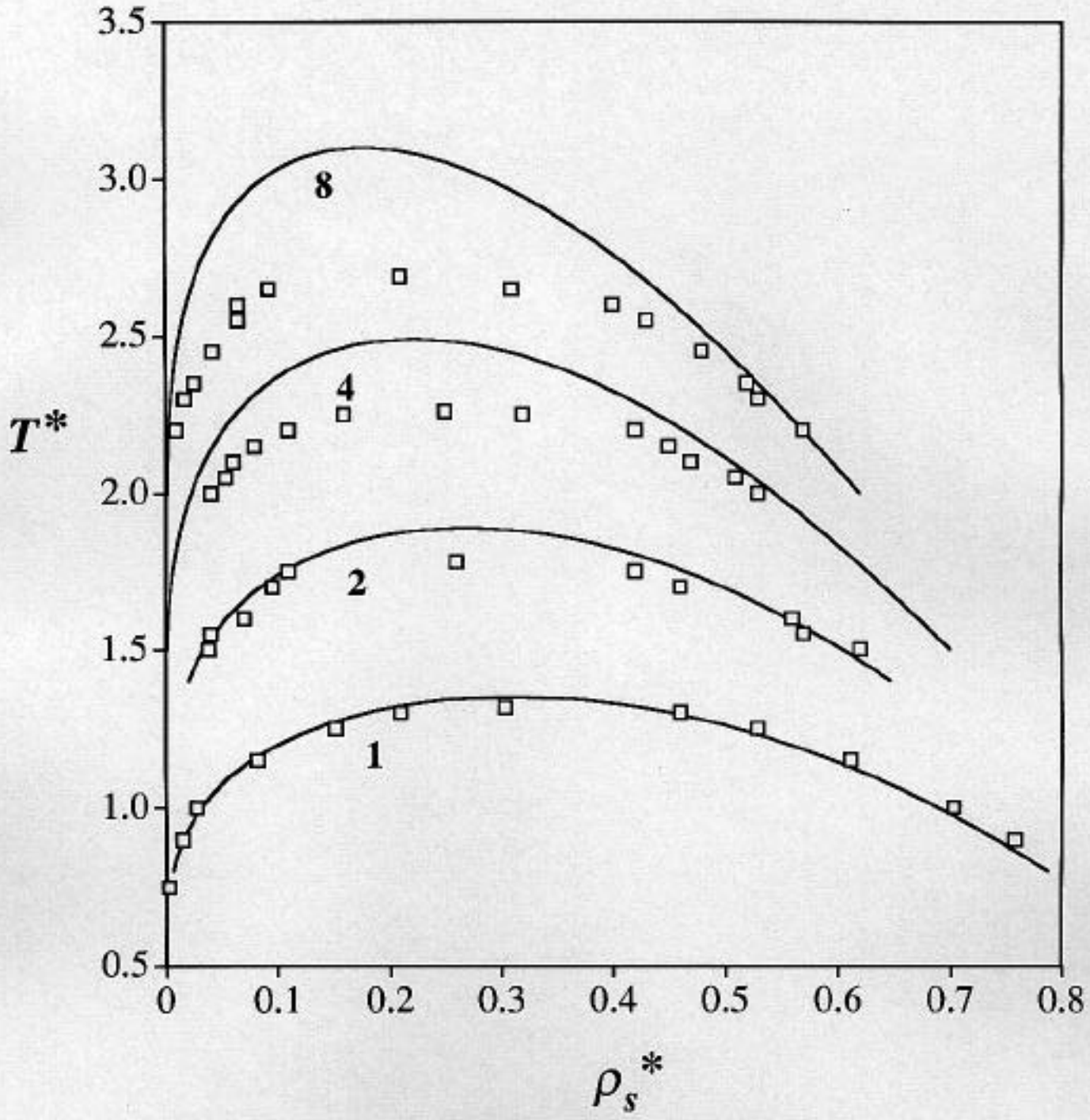
Figure Captions

Figure 1. The vapour-liquid coexistence densities for Lennard-Jones chains of length m_s compared with the Gibbs ensemble simulation data of Panagiotopoulos [31] ($m_s = 1$), and of Escobedo and de Pablo [25] (m_s =2, 4 and 8). The continuous curves correspond to the SAFT-VR approach, and each is labelled with the values of the chain length m_s. The reduced parameters used are $T^* = kT/\epsilon$ and $\rho_s^* = \rho_s\sigma^3$.

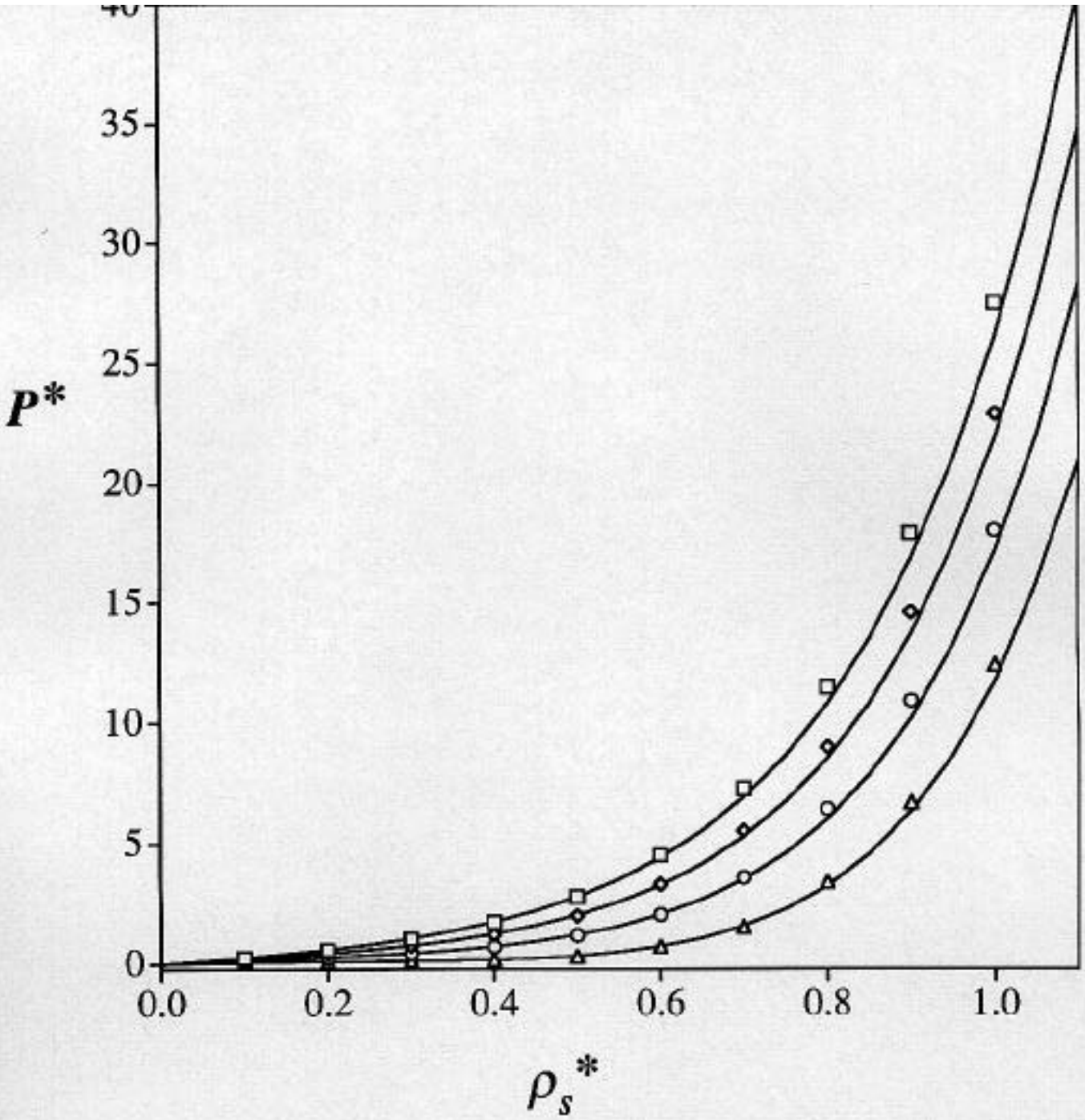
Figure 2. The reduced pressure $P^* = P\sigma^3/\epsilon$ of Lennard-Jones chains with $m_s = 2$ (diatomics) as a function of the reduced monomer density $\rho_s^* = \rho_s\sigma^3$. The squares, diamonds, circles and triangles are the molecular dynamics simulation results of Johnson *et al.* [24] for $T^* = kT/\epsilon$ =5, 4, 3 and 2, respectively. The continuous curves correspond to the SAFT-VR predictions.

Figure 3. The reduced pressure $P^* = P\sigma^3/\epsilon$ of Lennard-Jones chains with $m_s = 4$ as a function of the reduced monomer density $\rho_s^* = \rho_s\sigma^3$. The diamonds, circles and triangles are the molecular dynamics simulation results of Johnson *et al.* [24] for $T^* = kT/\epsilon$ =4, 3 and 2, respectively. The continuous curves correspond to the SAFT-VR prediction.

Figure 4. The reduced pressure $P^* = P\sigma^3/\epsilon$ of Lennard-Jones chains with $m_s = 8$ as a function of the reduced monomer density $\rho_s^* = \rho_s\sigma^3$. The diamonds, circles and triangles are the molecular dynamics simulation results of Johnson *et al.* [24] for $T^* = kT/\epsilon$ =4, 3 and 2, respectively. The continuous curves correspond to the SAFT-VR prediction.



Davies et al Figure 1



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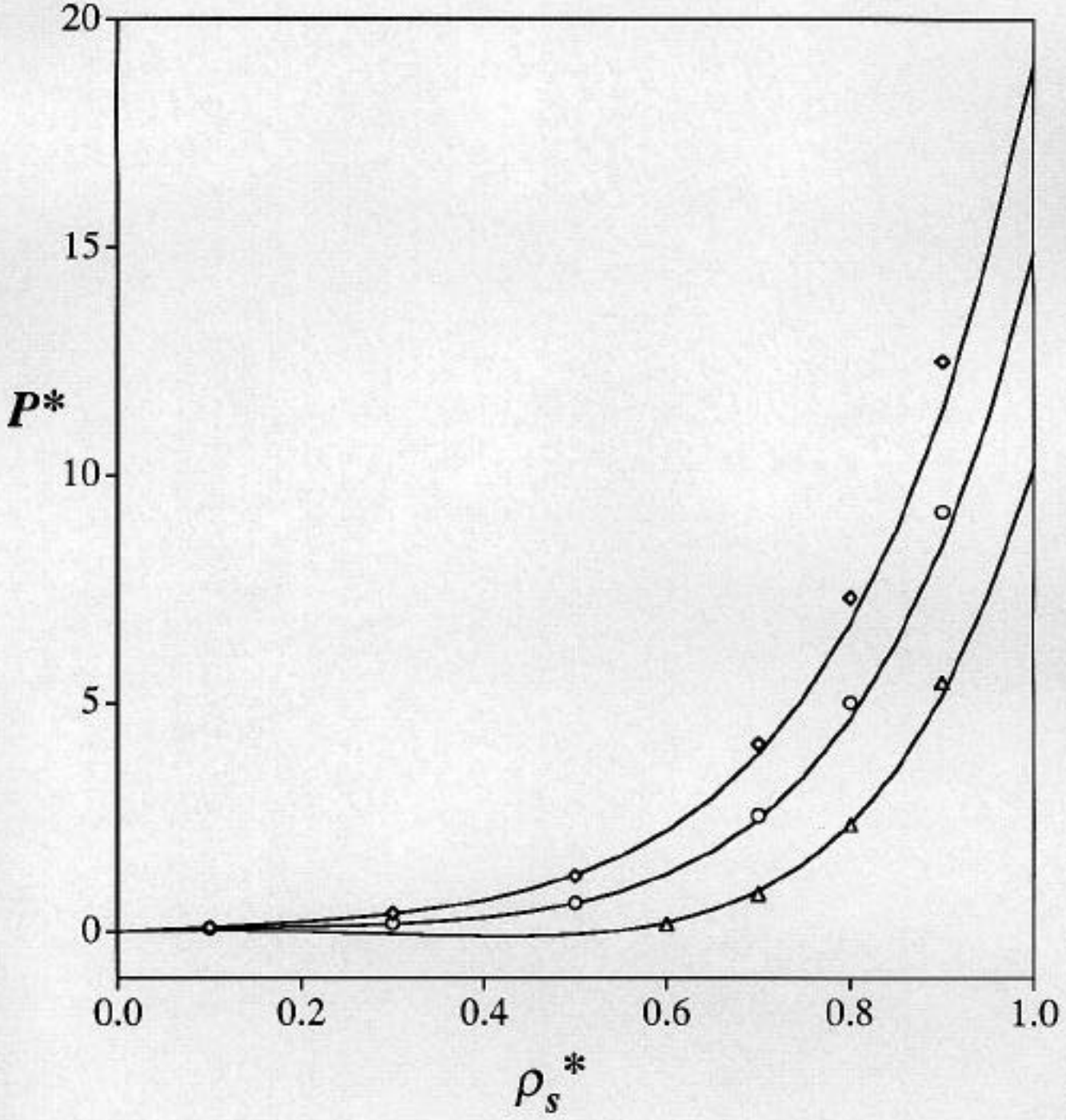
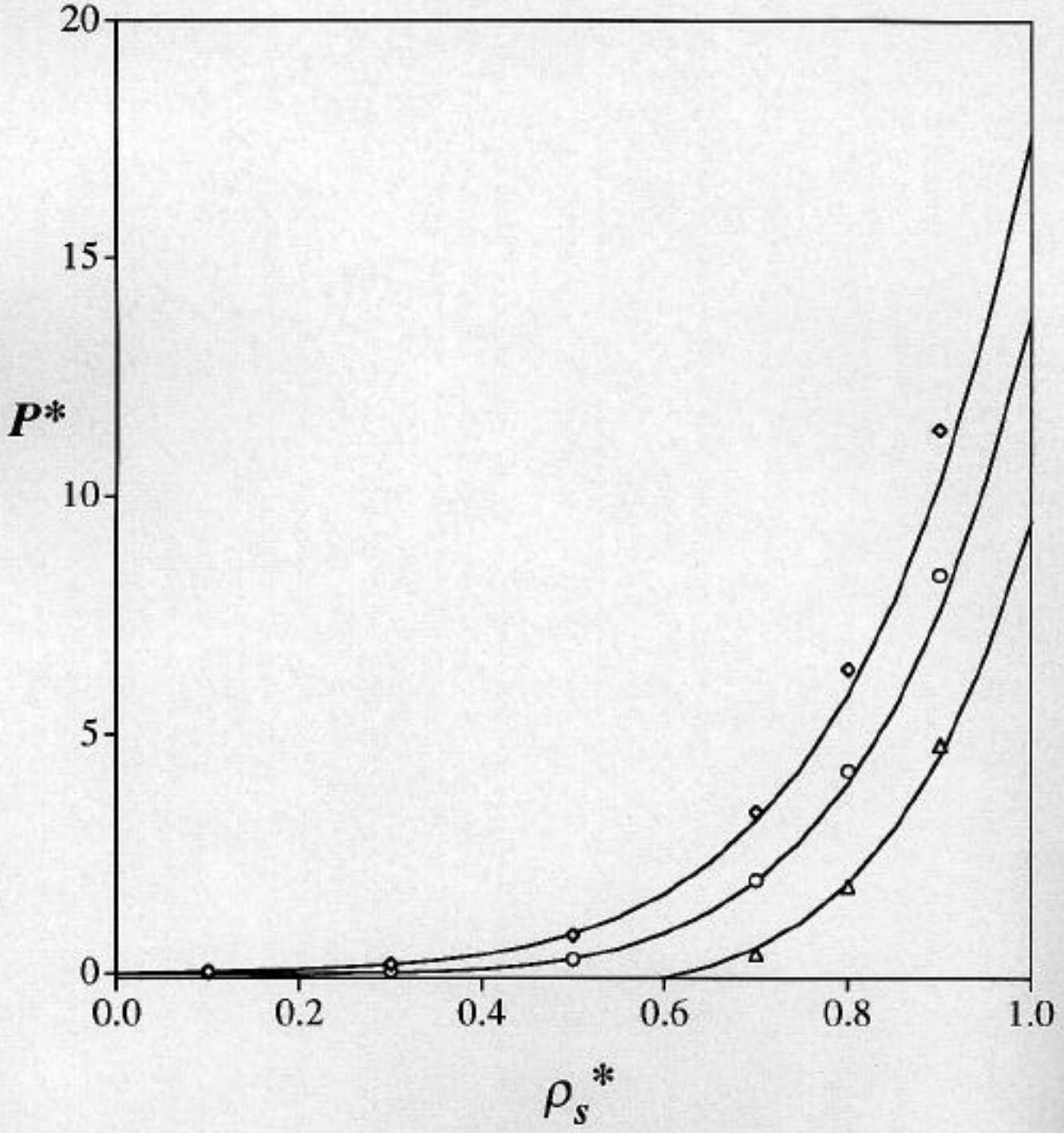


Davies et al. Figure 3



Davies et al Figure 4