

## Mixtures of associating spherical and chain molecules

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**Abstract** - Recently, we have investigated the effect of molecular association on the critical and phase coexistence properties of fluids with various off-centre attractive sites. The individual molecules are first represented by hard-sphere repulsive cores with square-well attractive sites, and a simple van der Waals mean-field term is also added to account for the dispersion forces. The equations can be extended to associating mixtures of spherical molecules with off-centre attraction sites. In the limit of complete bonding, chains of hard-spheres are formed. Expressions for mixtures of associating spherical molecules, pure hard-sphere chains and mixtures of chains, are reviewed. These equations are then used to study the effect of chain length on the phase equilibrium properties of non-associating chains. Quantitative comparisons of the theoretical results with experimental data are shown for the critical points of the n-alkane homologous series.

### INTRODUCTION

Binary and ternary mixtures of industrial interest often include components which associate strongly. Because no satisfactory theory of associating mixtures has been available, engineers and physical chemists in industry have adopted the chemical approach to such mixtures, in which chemical reactions are postulated to account for the formation of dimers, complexes, etc. This approach is useful as a method of correlating data, but is very limited in value as a predictive tool. Theories which are soundly based in statistical mechanics offer a viable alternative and have a greater predictive value. Here, we present a statistical mechanical equation of state for associating fluids. Asymmetries in the molecular shape are taken into account by considering chain molecules.

The effect of molecular association on the properties of fluids with highly directional attractive interactions, has recently been examined for systems of spherical (ref. 1) and chain-like (ref. 2) molecules. In the case of associating fluids of spherical molecules, two of the simplest cases were examined, namely, hard-sphere molecules with one or two off-centre square-well attraction sites. A simple and successful theory based on a resummed cluster expansion (ref. 3-6) was used to calculate the thermodynamic properties of these systems. The results of the theory were shown to be in good agreement with computer simulation data for hard-spheres with one or two sites (ref. 1). By adding a van der Waals attractive term, the phase equilibria of the associating fluids were then determined using the theory for various values of the strength and range of the bonding sites.

Expressions for chains of hard spheres can be obtained in the limit of complete bonding. In the case of homonuclear chains of hard spheres, the separate effects of molecular association and chain size on the coexistence properties have also been investigated (ref. 2). The hard-chain properties calculated from the theory are also shown to be in good agreement with existing computer simulation results.

In this paper we review the basic expressions for mixtures of associating spherical molecules. By generalizing the approach to associating hard-sphere mixtures, the expressions for chains of hard spheres can be derived. Hence, accurate equations of state for homonuclear hard-sphere chains and mixtures of chains are obtained. The hard spheres making up a given chain in the mixture are taken to be the same size, but the spheres of other chains can be of a different size and the chains can be of a different length.

The equations derived for the hard-chain fluids are used to study the effect of chain length on the critical properties of non-associating chain molecules, and comparisons are made with experimental data for the homologous series of the n-alkanes. The effect of the chain length on the phase equilibria of chain molecules is also shown.

## THEORY

## Associating fluid mixtures

A qualitative explanation of the approach for mixtures with single bonding sites has been given by Joslin et al. (ref. 7). Comparison of results from the theory and computer simulation for binary mixtures of equal-sized hard spheres A and B in which only AB dimers can form, were presented and excellent agreement was found. The expressions have subsequently been generalized to mixtures with multiple bonding sites (ref. 8 and ref. 2).

The equation of state of an associating fluid mixture of molecules with multiple bonding sites can be written as a sum of separate contributions. For the compressibility factor we have

$$Z^{Mix} = \frac{P}{\rho kT} = Z_R^{Mix} + Z_{MF}^{Mix} + Z_{bond}^{Mix}, \quad (1)$$

where  $P$  is the pressure,  $T$  the temperature,  $\rho$  the total number density, and  $k$  is Boltzmann's constant. Here,  $Z_R^{Mix}$  is the compressibility factor due to the repulsive cores,  $Z_{MF}^{Mix}$  is the mean-field contribution to the free energy due to the dispersion forces, and  $Z_{bond}^{Mix}$  is the change due to bonding.

In the case of mixtures of hard spheres, the reference term  $Z_R^{Mix} = Z_{HS}^{Mix}$  can be obtained from the equation of Mansoori et al. (ref. 9 and ref. 10),

$$Z_{HS}^{Mix} = \frac{6}{\pi\rho} \left[ \frac{\zeta_0}{1-\zeta_3} + \frac{3\zeta_1\zeta_2}{(1-\zeta_3)^2} + \frac{3\zeta_2^3}{(1-\zeta_3)^3} - \frac{\zeta_3\zeta_2^3}{(1-\zeta_3)^3} \right], \quad (2)$$

where

$$\zeta_l = \frac{\pi\rho}{6} \sum_{\beta} X^{(\beta)} (\sigma_{\beta})^l. \quad (3)$$

The sum in equation (3) is over all the hard-sphere components  $\beta$ ,  $X^{(\beta)}$  is the mole fraction of component  $\beta$ , and  $\sigma_{\beta}$  is the hard-sphere diameter of spheres  $\beta$ .

$Z_{MF}^{Mix}$  of equation (1) is the mean-field contribution to the compressibility factor due to the dispersion forces, for which the simplest approximation is a generalized van der Waals term,

$$Z_{MF}^{Mix} = -\frac{\rho}{kT} \sum_{\gamma} \sum_{\beta} X^{(\gamma)} X^{(\beta)} a_{\gamma\beta}. \quad (4)$$

Here, the sums are over all components in the mixture, and the constants  $a_{\gamma\beta}$  are measures of the strengths of the mean-field attractions between components  $\gamma$  and  $\beta$ . More accurate expressions for the mean-field term derived from perturbation theory may also be used.

Finally,  $Z_{bond}^{Mix}$  is the change due to bonding, which is given by (ref. 2)

$$Z_{bond}^{Mix} = \rho \sum_{\beta} X^{(\beta)} \left\{ \sum_{A \in \Gamma^{(\beta)}} \left( \frac{\partial X_A^{(\beta)}}{\partial \rho} \right)_{T,N} \left[ \frac{1}{X_A^{(\beta)}} - \frac{1}{2} \right] \right\}. \quad (5)$$

$\Gamma^{(\beta)}$  is the set of bonding sites on a molecule of component  $\beta$ , and  $X_A^{(\beta)}$  is the fraction of component  $\beta$  not bonded at a given site A. The first sum in equation (5) is over all components  $\beta$ , and the second sum is over all sites in the set  $\Gamma^{(\beta)}$ . The  $X_{As}$  are obtained from the equation

$$X_A^{(\beta)} = \left[ 1 + \rho \sum_{\gamma} \sum_{B \in \Gamma^{(\gamma)}} X^{(\gamma)} X_B^{(\gamma)} \Delta_{AB}^{(\beta\gamma)} \right]^{-1}, \quad (6)$$

where  $\Delta_{AB}^{(\beta\gamma)}$  is defined by

$$\Delta_{AB}^{(\beta\gamma)} = \int g_R^{(\beta\gamma)}(12) f_{AB}^{(\beta\gamma)}(12) d(12). \quad (7)$$

$f_{AB}^{(\beta\gamma)}(12) = \exp(-\phi_{AB}^{(\beta\gamma)}(12)/kT) - 1$  is the Mayer  $f$ -function of the highly anisotropic, short-ranged site-site attractions, and  $g_R^{(\beta\gamma)}(12)$  is the reference fluid pair correlation function. The notation (12) represents the positions and orientations of molecules 1 and 2, and  $\int d(12)$  denotes an unweighted average over all orientations of molecules 1 and 2 and integration over all separations of molecules 1 and 2.

The properties of the associating mixture can be calculated from a knowledge of the pair distribution function  $g_R^{(\beta\gamma)}$  (12) of the repulsive reference fluid. For hard-sphere mixtures the distribution functions can be obtained using Perram's method (ref. 11), with the Verlet-Weis (ref. 12) correction to ensure good agreement with computer simulation data. Once  $g_R^{(\beta\gamma)}$  (12) is available, equation (7) can be integrated numerically to give  $\Delta_{AB}^{(\beta\gamma)}$ , and equation (6) can then be solved iteratively for the fractions of sites that are not bonded at given sites. Finally, the change in the compressibility factor due to bonding is obtained using equation (5) with the values of  $X_A^{(\beta)}$  calculated for all the sites of set  $\Gamma^{(\beta)}$  on each component.

The above expressions provide a representation of the properties of associating mixtures of spherical or nearly spherical molecules. Reference equations for fluids composed of chains of hard spheres are presented in the following section in order to deal with the effect of shape as well as the effect of bonding.

### Chains of hard spheres

Chains of hard spheres can be constructed by bonding together the spheres of an  $M$ -component hard-sphere mixture (ref. 2). The appropriate spheres are bonded together to form  $r$  chains of  $m_1, m_2, \dots, m_r$  spheres with  $M = \sum_{i=1}^r m_i$ . We assume that only homonuclear chains are formed, i.e. all the spheres making up a given chain are of identical size.

The equation of state for mixtures of homonuclear hard-sphere chains can be written as

$$Z_{HC}^{Mix} = Z_{HS}^{Mix} + Z_{chain}^{Mix}. \quad (8)$$

$Z_{HS}^{Mix}$  is the compressibility factor of the hard-sphere mixture which is given by equation (2), and  $Z_{chain}^{Mix}$ , the change in the compressibility factor due to the formation of a mixture of hard-sphere chains. The latter is obtained as a special limiting case of equation (5) (ref. 2),

$$Z_{chain}^{Mix} = - \sum_{i=1}^r \frac{\rho_c^{(i)}}{\rho} (m_i - 1) \left\{ 1 + \rho \left( \frac{\partial \ln g_{HS}^{(ii)}(\sigma_{ii})}{\partial \rho} \right) \right\}. \quad (9)$$

Here, the sum is over each chain  $i$  ( $m_i$  hard spheres) in the mixture.  $Z_{chain}^{Mix} = P/(\rho kT)$  is expressed in terms of the total number density of spheres, and  $\rho_c^{(i)}$  is the number density of chain  $i$ .  $g_{HS}^{(ii)}(\sigma_{ii})$  is the contact value of the pair correlation function for like-sized hard spheres in a hard-sphere mixture, and  $\sigma_{ii}$  is the diameter of the hard spheres making up chain  $i$ . For a hard-sphere mixture,  $g_{HS}^{(ii)}(\sigma_{ii})$  is given accurately by (ref. 10 and ref. 13)

$$g_{HS}^{(ii)}(\sigma_{ii}) = \frac{1}{1 - \zeta_3} + \frac{3\sigma_{ii}\zeta_2}{2(1 - \zeta_3)^2} + \frac{\sigma_{ii}^2\zeta_2^2}{2(1 - \zeta_3)^3}, \quad (10)$$

where

$$\zeta_i = \frac{\pi}{6} \sum_i \rho_c^{(i)} m_i (\sigma_{ii})^i. \quad (11)$$

Since the chains are homonuclear, the sum of equation (11) has been written as a sum over chains. The changes in the free energy and chemical potentials due to chain formation are obtained through the usual thermodynamic relations.

The expressions for mixtures of hard-sphere chains can now be used as the repulsive reference term in equation (1),  $Z_R^{Mix} = Z_{HC}^{Mix}$ . In this way, associating mixtures of chain molecules can be investigated to determine the separate effects of association and chain size on the system's properties.

The equation of state for a pure fluid of homonuclear hard-sphere chains is obtained as a special case of equation (8),

$$Z_{HC} = Z_{HS} + Z_{chain}. \quad (12)$$

$Z_{HS}$  is given by the equation of Carnahan and Starling (ref. 14),

$$Z_{HS} = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3}, \quad (13)$$

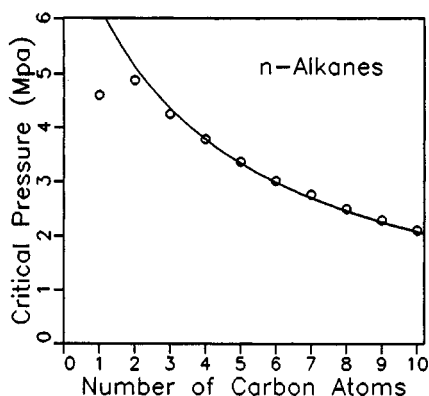


Fig. 1.

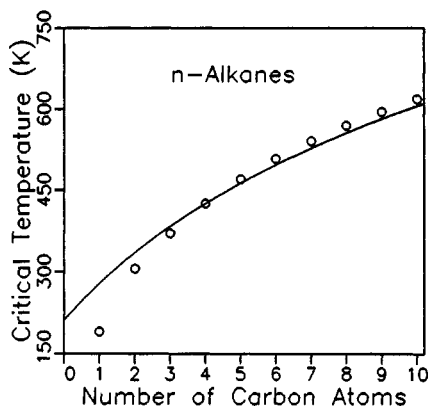


Fig. 2.

Fig. 1. The critical pressure,  $P_c$  (MPa), as a function of carbon number for the homologous series of the normal alkanes. The experimental results shown as the data points are obtained from ref. 21, and the solid curve is obtained theoretically using equation (16) by fitting to the critical point of n-butane.

Fig. 2. The critical temperature,  $T_c$  (K), as a function of carbon number for the homologous series of the normal alkanes. The theoretical results are fitted to the critical point of n-butane, and are compared with experimental data.

where the reduced density  $\eta = b\rho$ ,  $b = \pi\sigma^3/6$ , and  $\sigma$  is the hard-sphere diameter.  $Z_{chain}$  for chains made up of  $m$  hard spheres is obtained from expression (9),

$$Z_{chain} = -\frac{m-1}{m} \left\{ 1 + \rho \left( \frac{\partial \ln g_{HS}(\sigma)}{\partial \rho} \right) \right\}, \quad (14)$$

and the contact value  $g_{HS}(\sigma)$  is determined from the virial equation (ref. 15),

$$g_{HS}(\sigma) = \frac{Z_{HS} - 1}{4\eta}. \quad (15)$$

The hard-chain compressibility factor becomes

$$Z_{HC} = Z_{HS} + Z_{chain} = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} - \frac{m-1}{m} \frac{1 + \eta - \eta^2/2}{(1 - \eta)(1 - \eta/2)}. \quad (16)$$

Here,  $m$  is the number of spheres in the chain and  $\eta$  is the reduced density of spheres. The compressibility factors of the hard-sphere chains and chain mixtures are expressed in terms of the total number of spheres in the system and not the number of chains.

Existing computer simulation data for the hard-disphere system ( $m = 2$ ) (ref. 16), and for flexible chains made up of 4, 8 and 16 tangent hard-spheres (ref. 17) have been shown to be in good agreement with the results of equation (16) (refs. 2 and 18). The equation is a good representation of hard-chain properties even for chains of eight spheres, although its adequacy decreases as the chains get longer. This is because the effect of the chain's steric self-hindrance is not taken into account, so that structural isomers of a given chain are treated in the same way (ref. 2).

Equation (16) is used in the following section to calculate the phase equilibrium properties of non-associating fluids of chain molecules. In order to study the coexistence properties of chain molecules, a mean-field contribution must be added to the repulsive hard-chain reference term. The equation of state for such a fluid can be written as

$$Z = Z_{HC} + Z_{MF}. \quad (17)$$

The hard-chain repulsive term  $Z_{HC}$  for homonuclear chains of  $m$  hard spheres is given by equation (16). The simplest approximation for the mean-field contribution to the compressibility factor is a

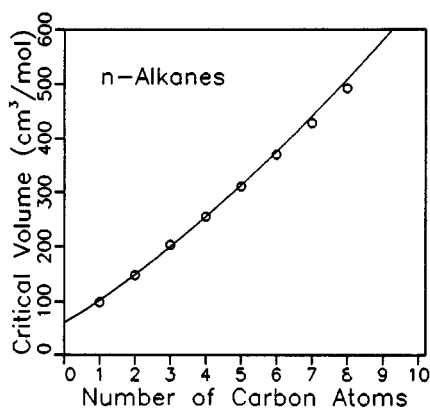


Fig. 3.

Fig. 3. The critical volume,  $V_c$  ( $\text{cm}^3/\text{mol}$ ), as a function of carbon number for the homologous series of the normal alkanes. The theoretical results are fitted to the critical point of n-butane, and are compared with experimental data.

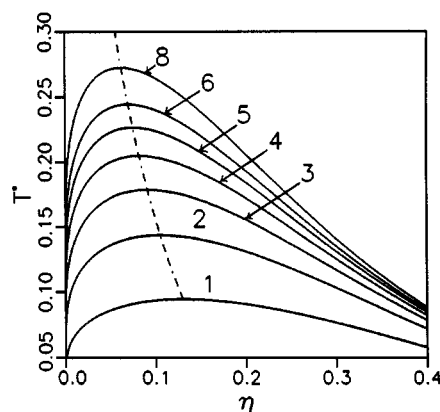


Fig. 4.

Fig. 4. Coexisting vapour and liquid densities,  $\eta$ , as a function of the reduced temperature,  $T^*$ , for non-associating chains of hard spheres with mean-field attractive interactions. The curves are labelled with the number of spheres  $m$  in the chain, and the locus of the critical point for different values of  $m$  is shown by the dashed curve.

van der Waals term,

$$Z_{MF} = -\frac{\epsilon_{MF}\eta}{kT}, \quad (18)$$

where the constant  $\epsilon_{MF}$  is a measure of the strength of the mean-field forces. The reduced density of spheres in the chains is used to calculate the mean-field contribution. In this approximation to the mean-field term, we assume that each sphere in the chain contributes equally to the mean-field energy. Although this approach means that the intramolecular mean-field interactions between spheres on the same chain are included, in the thermodynamic limit ( $N \rightarrow \infty$ ) the mean-field interactions between spheres on different chains greatly out-weigh the intramolecular contribution.

## RESULTS

For a pure fluid at coexistence, the pressure, temperature and chemical potential of the vapour and liquid phases must be equal, i.e.  $P_v = P_l$ ,  $T_v = T_l$ , and  $\mu_v = \mu_l$ . At the critical point, the first and second derivatives of the pressure with respect to volume are zero. When the equation of state for the hard-chain fluid (equation (17)) is solved numerically to satisfy these conditions, the critical point and coexistence curves are established for a given value of the chain size  $m$ . In the phase equilibrium calculations, it is useful to reduce the temperature with respect to the mean-field constant  $\epsilon_{MF}$ ,  $T^* = kT/\epsilon_{MF}$ . The pressure is also written in terms of  $\epsilon_{MF}$  and the hard-sphere diameter  $\sigma$  of the spheres making up the chain, i.e.  $P^* = bP/\epsilon_{MF}$ .

We have used equation (17) to predict the critical points for the homologous series of the normal paraffin hydrocarbons ( $\text{C}_n\text{H}_{2n+2}$ ). The carbon-carbon bond length for the n-alkanes is about 1.5 Å (ref. 19), whilst the Lennard-Jones diameter for methane is of the order of 3.8 Å (ref. 20). Hence, the carbon-carbon separation is about one-third the diameter of a methane molecule. In terms of the hard-chain equation, if methane is modelled as a spherical molecule with  $m = 1$ , then ethane can be modelled as two interpenetrating spheres with  $m = 1 + 1/3$ , propane will have a chain size of  $m = 1 + 2/3$ , n-butane will be represented by  $m = 2$  etc. In general,  $\text{C}_n\text{H}_{2n+2}$  will have a corresponding chain size of  $m = 1 + (n - 1)/3$ . Although this is quite a crude approximation, it is found to give reasonable results. The assumption that the hard-chain equation can be used to interpolate the properties of systems of interpenetrating spheres still has to be examined.

The critical points of the n-alkanes predicted using the theory are compared with experimental data (ref. 21) as shown in Figs. 1-3. The theoretical curves have been fitted to the critical point of n-butane ( $T_c = 425.14$  K,  $P_c = 3.784$  MPa, and  $V_c = 255$   $\text{cm}^3/\text{mol}$ ) (ref. 21). The choice of n-butane is arbitrary, and is due to the fact that n-butane lies in the middle of the series of the alkanes investigated here. In Fig. 1 we show the critical pressure  $P_c$ , for the n-alkane homologous

series as a function of the carbon number,  $n$ . The experimental data are shown as circles and the solid curve is obtained from the theory using equation (17). Although the agreement between theory and experiment is reasonably good for ethane and higher homologues, the theory does not accurately predict the critical point of methane. The experimental critical pressure of methane is lower than that of ethane, opposing the trend of a decrease in the critical pressure with increasing carbon number for the higher n-alkanes. A similar agreement is shown for critical temperature,  $T_c$ , in Fig. 2; the theory again fails with methane but does reasonably well with the higher carbon numbers. It is difficult to say whether these shortcomings are due to the hard-chain reference term or the mean-field term. The anomalous behaviour found for methane seems to be due to the fact that in going from methane to ethane there is a much larger change in the critical point than the change found for any other pair of alkanes. It is rather surprising, however, that the predictions of the hard-chain equations for the critical volume,  $V_c$ , are in very good agreement with the corresponding experimental values for all the n-alkanes studied, including methane (see Fig. 3).

Equation (17) has also been used to determine the phase equilibria of model fluids of chain molecules. The densities,  $\eta$ , of the coexisting vapour and liquid phases are plotted as a function of temperature,  $T^*$ , in Fig. 4. The coexistence curves are shown for various values of the chain length  $m$ . An increase in chain length has two major effects on the coexistence curve. Firstly, the critical temperature,  $T_c^*$ , increases as  $m$  is increased; for the monomer sphere fluid  $m = 1$ ,  $T_c^* = 0.0943287$ , whilst for  $m = 8$ ,  $T_c^* = 0.273016$ . The second effect is the decrease in the critical density with increasing chain length; a value of  $\eta_c = 0.130444$  when  $m = 1$  decreases to  $\eta_c = 0.0622828$  when  $m = 8$ . The combined result of these two effects is that the coexistence curves are shifted to higher temperatures and lower densities.

### CONCLUSION

We have presented an equation of state for associating fluid mixtures with multiple bonding sites. Initially, associating mixtures of spherical molecules were examined. The approach was extended to systems of homonuclear hard-sphere chains and mixtures of chains to deal with the effect of shape as well as association. In future work, we will use these equations to determine the phase diagrams for binary and ternary associating mixtures of industrial interest. The equation of state for fluids of chain molecules was used to predict the critical properties of the homologous series of the n-alkanes. A reasonably good agreement between theory and experiment was obtained. The phase equilibria of model non-associating chain molecules were also determined, and were shown to depend critically on the chain length (see Fig. 4).

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