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Phase Equilibria of Associating Fluids of Spherical and Chain Molecules[1]

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The development of equations of state for strongly associating fluids and fluid mixtures has proved over the years to be a difficult problem. The first-order perturbation theory solution of a resummed cluster expansion has been used to investigate the effect of molecular associations on the critical and phase coexistence properties of fluids with one and two off-center attractive sites. The individual molecules are represented by hard-sphere repulsive cores with square-well attractive sites. Model systems comprising chains of hard spheres have also been examined. Isothermal–isobaric Monte Carlo simulations of hard-sphere fluids with one and two attractive sites are shown to be in good agreement with the results of the theory. A simple van der Waals mean-field term is also added to account for the dispersion forces. The critical points and phase equilibria of the associating fluids are determined for various values of the strength and range of the attractive site, as well as for different chain lengths. The theory can treat fluids with strong hydrogen-bonding associations such as the carboxylic acids the aliphatic alcohols, hydrogen fluoride, water, etc.

KEY WORDS: associating fluids; computer simulations; equation of state; mixtures; perturbation theory; phase equilibrium.

1. INTRODUCTION

Binary and ternary mixtures of industrial interest often include components which associate strongly with themselves and/or each other. Examples of these systems are the aliphatic alcohol–alkane, alkane–water, alcohol–water, alcohol–aromatic, and water–aromatic mixtures; typical ternary systems are the alkane–alcohol–water and aromatic–alcohol–water

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mixtures. The phase equilibria of such mixtures are richly complex, with varying degrees of liquid–liquid immiscibility including closed-loop immiscibility.

Whereas fairly simple theories provide a good description of nonpolar and weakly polar fluids, theories for strongly polar and associating fluids have met with only limited success. The chemical theory of solutions first developed by Dolezalek [1, 2] is the oldest method for treating associating mixtures. It postulates the existence of distinct molecular species in solution, which are assumed to be in chemical equilibrium. An important disadvantage of this approach lies in the arbitrary way in which one decides which species are present. After assuming the equilibrium scheme, one is then faced with the problem of determining the equilibrium constants together with their temperature dependences. An alternative approach is that of the lattice theories, which consider the structure of the liquid to be solid-like in character. Equations of state based on lattice theories [2] have been applied, with varying degrees of success, to a wide variety of nonelectrolyte liquid mixtures containing nonpolar and polar fluids. However, the underlying concept of representing a liquid's structure by a lattice is a vast oversimplification, and important density and entropy effects cannot be accounted for. Thus, lattice theories are limited mainly to predicting the basic qualitative features of a system's properties.

A more promising route leading to an understanding of associating fluids involves theories which are firmly based in statistical mechanics. The strong, anisotropic molecular interactions found in these systems are incorporated in the foundations of the theory by using simple, well-defined potential models. Recently, a theory has been proposed by Wertheim [3] to deal with these interactions in a simple way. Wertheim's theory is based on a resummed cluster expansion which is made in terms of two densities, the usual density ρ, and the monomer density ρ_0. The complex graphical expansions can be simplified by assuming that the repulsive cores restrict the orientationally dependent attractive forces to only dimer formation at each bonding site. As a result, the final expression takes the form of a thermodynamic perturbation theory which is relatively simple to use. This approach has been used to deal with spherical molecules with multiple bonding sites. We have also extended the theory to chain molecules and to associating mixtures.

2. SPHERICAL MOLECULES

The compressibility factor $Z = P/(\rho kT)$ (P is the pressure, T the temperature, ρ the number density, and k Boltzmann's constant) for an associating fluid of spherical molecules can be written as a sum of separate contributions

$$Z = Z_{\mathrm{HS}} + Z_{\mathrm{MF}} + Z_{\mathrm{bond}} \tag{1}$$

Here, Z_{HS} is the compressibility factor due to the hard-sphere repulsive cores, Z_{MF} is the mean-field contribution to the free energy due to the dispersion forces, and Z_{bond} is the change due to bonding.

The hard-sphere compressibility is accurately given by the equation of Carnahan and Starling [4]

$$Z_{\mathrm{HS}} = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} \tag{2}$$

in terms of the reduced density $\eta = (\pi/6)\, \rho\sigma^3$, where σ is the hard-sphere diameter.

The simplest approximation for the mean-field contribution to the compressibility factor is the van der Waals term

$$Z_{\mathrm{MF}} = -\frac{\varepsilon_{\mathrm{MF}}\eta}{kT} \tag{3}$$

where the constant $\varepsilon_{\mathrm{MF}}$ is a measure of the strength of the mean-field forces.

For a one-component system with M bonding sites, the change in the compressibility factor due to bonding can be obtained from Wertheim [3]:

$$Z_{\mathrm{bond}} = \sum_{A \in \Gamma} \eta \left(\frac{\partial X_{\mathrm{A}}}{\partial \eta} \right)_{T,N} \left(\frac{1}{X_{\mathrm{A}}} - \frac{1}{2} \right) \tag{4}$$

Here, we have used Chapman's simpler notation [5], where X_{A} is the fraction of molecules *not* bonded at a given site A. The summation in Eq. (4) is over all sites A in the set Γ (M in all). The individual X_{A} values are obtained from

$$X_{\mathrm{A}} = \left[1 + \sum_{B \in \Gamma} \rho X_{\mathrm{B}} \Delta_{\mathrm{AB}} \right]^{-1} \tag{5}$$

where Δ_{AB} is defined by

$$\Delta_{\mathrm{AB}} = \int g_{\mathrm{HS}}(12)\, f_{\mathrm{AB}}(12)\, d(12) \tag{6}$$

$g_{\mathrm{HS}}(12)$ is the reference-fluid distribution function, $f_{\mathrm{AB}} = \exp[-\phi_{\mathrm{AB}}(\vec{r}_{\mathrm{AB}})/kT] - 1$ is the Mayer f function, ϕ_{AB} is the site–site attractive interaction, and $d(12)$ denotes an integration over all orientations and separations of molecules 1 and 2.

The integration involved in Eq. (6) for Δ_{AB} can be performed numerically by using the Verlet–Weis prescription for the hard-sphere distribution function [6] adjusted to fit simulation data. Alternatively, an approximate analytic expression for Δ_{AB} can be used. If we assume that $r^2 g_{\mathrm{HS}}(r)$ is constant and equal to the value at contact $\sigma^2 g_{\mathrm{HS}}(\sigma)$ over the short range of the site–site potential, Δ_{AB} can be written [7]

$$\Delta_{\mathrm{AB}} = 4\pi g_{\mathrm{HS}}(\sigma)\, K_{\mathrm{AB}} F_{\mathrm{AB}} \tag{7}$$

This expression was derived for a system with square-well bonding sites, where $F_{\mathrm{AB}} = \exp(\varepsilon_{\mathrm{AB}}/kT) - 1$, and each AB site–site interaction is characterized by the square-well depth $-\varepsilon_{\mathrm{AB}}$. $g_{\mathrm{HS}}(\sigma)$ is obtained from the virial equation [8], $g_{\mathrm{HS}}(\sigma) = (Z_{\mathrm{HS}} - 1)/4\eta$, and K_{AB} is an integral which measures the volume available for bonding to sites A and B on molecules 1 and 2 (see Ref. 7 for a precise definition in terms of a given potential model). In general, the solution of Eq. (5) for X_{A} is found using an iterative procedure; however, in the special cases of molecules with one or two attractive sites an analytic expression can be written.

Computer simulations which accurately calculate the thermodynamic properties of a fluid with a specified potential model can be used to test the theory. Isothermal–isobaric (NPT) Monte Carlo (MC) simulations were performed for hard spheres with square-well bonding sites of energy $-\varepsilon_{\mathrm{site}}$ and with a bonding volume K. For the system with one bonding site $\varepsilon_{\mathrm{site}} = 7kT$ and $K = 1.485 \times 10^{-4}\,\sigma^3$. In the case of the system with two bonding sites, the sites were placed on directly opposite sides of the sphere, and $\varepsilon_{\mathrm{site}} = 5kT$ and $K = 2.970 \times 10^{-4}\,\sigma^3$. These values were chosen for the parameters of the site–site potential because they give physically reasonable results for real systems which can be modeled by molecules with one and two bonding sites. The actual potential model used is described in more detail elsewhere [7].

In Fig. 1 for the fraction of molecules present as monomers, X, we compare the results of NPT MC simulations with the corresponding results calculated using the theory [7]. As mentioned earlier, the calculation of Δ_{AB} and X requires the hard-sphere radial distribution function. The solid curves in these figures are obtained using the Verlet–Weis [6] hard-sphere distribution function, and the dashed curves are obtained using the alternative analytic expression for Δ_{AB}, Eq. (7). The theoretical results for a hard-sphere system with one (Fig. 1a) and two (Fig. 1b) attractive sites are in good agreement with the simulation data. As expected, the monomer concentration decreases with density as more and more bonding takes

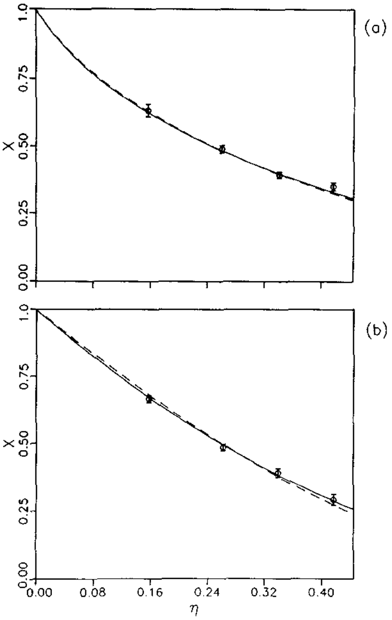

Fig. 1. The mole fraction of monomers X from NPT Monte Carlo simulations (circles), theory (solid curve), and the approximate solution to the theory (dashed curve). (a) Hard spheres with one bonding site, $\varepsilon_{\mathrm{site}} = 7kT$ and $K = 1.485 \times 10^{-4}\sigma^3$. (b) Hard spheres with two bonding sites, $\varepsilon_{\mathrm{site}} = 5kT$ and $K = 2.970 \times 10^{-4}\sigma^3$.

place. In the case of the one-site system, the curves calculated from Eq. (7) (dashed curves) are virtually indistinguishable from those of the exact numerical integration (solid curves).

The equation of state for a fluid of hard spheres with anisotropic attraction sites was given by Eq. (1). We have calculated the coexistence properties of the associating hard-sphere fluids with one or two bonding sites for various values of the site–site square-well interaction strength $\varepsilon_{\mathrm{site}}$ reduced with respect to the mean-field energy, $\varepsilon^*_{\mathrm{site}} = \varepsilon_{\mathrm{site}}/\varepsilon_{\mathrm{MF}}$. In every case the bonding volume was given the value of $K^* = 4.424 \times 10^{-5}$, where $K^* = K/\sigma^3$.

The densities of the coexisting vapor and liquid phases are shown in Fig. 2 as a function of the reduced temperature $T^* = kT/\varepsilon_{\mathrm{MF}}$ for the one-site system. The curves denoted by 0 and ∞ represent the limits of no association and full association, respectively. Systems with intermediate values of $\varepsilon^*_{\mathrm{site}}$ have also been investigated; one can see that the main effect

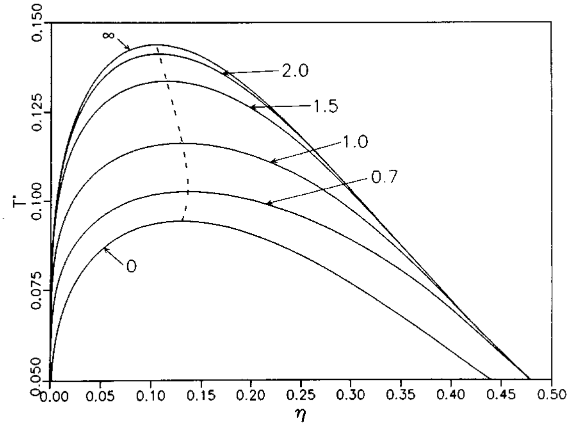

Fig. 2. Coexisting vapor and liquid densities η as a function of the reduced temperature T^* for hard-sphere fluids with one bonding site. The curves are labeled with the corresponding values of $\varepsilon^*_{\text{site}}$, and in all cases the bonding volume is $K^* = 4.424 \times 10^{-5}$. The locus of the critical point for different values of $\varepsilon^*_{\text{site}}$ is shown by the dashed curve.

of a strong association is to increase the critical temperature and hence the range of vapor–liquid coexistence. The dashed line shown in Fig. 2 represents the locus of the critical point. The corresponding coexistence curves for a hard-sphere fluid with two bonding sites A and B, where only AB bonding is allowed, are shown in Fig. 3. The effect of having two

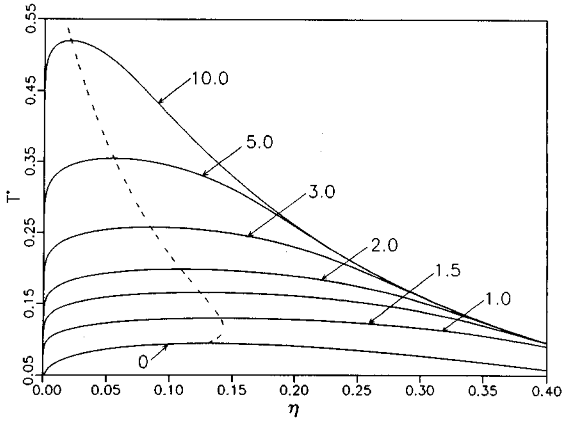

Fig. 3. Coexisting vapor and liquid densities η as a function of the reduced temperature T^* for the hard-sphere systems with two bonding sites. The curves are labeled with the corresponding values of $\varepsilon^*_{\text{site}}$, and in all cases the bonding volume is $K^* = 4.424 \times 10^{-5}$.

bonding sites shifts the coexistence curves to much higher temperatures than for the system with one bonding site. In the case of the one-site system, the phase behavior lies somewhere between the discrete limits of no association and full dimerization. The situation is quite different for an associating fluid with two bonding sites, since the molecules can associate to form chains of any length.

3. CHAIN MOLECULES

The compressibility factor $Z_{\mathrm{HC}} = P/(\rho kT)$ for homonuclear chain molecules made up of m hard spheres is given by [9]

$$Z_{\mathrm{HC}} = \frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3} - \frac{m-1}{m}\,\frac{1+\eta-\eta^2/2}{(1-\eta)(1-\eta/2)} \tag{8}$$

where $\eta = (\pi/6)\,\rho\sigma^3$ is the reduced density of spheres. This equation is obtained by using Wertheim's theory to bond spheres into chains. For the hard-chain system the second virial coefficient is determined from Eq. (8) as

$$\begin{aligned} B_2 &= \left(\frac{\partial Z_{\mathrm{HC}}}{\partial \rho}\right)\bigg|_{\rho=0} \\ &= \frac{m^2\pi\sigma^3}{6}\left[4 - \frac{5}{2}\left(\frac{m-1}{m}\right)\right] \end{aligned} \tag{9}$$

In the case of an infinitely long chain ($m \to \infty$) the second virial coefficient becomes

$$B_2 = \frac{L^2\sigma\pi}{4} \tag{10}$$

where the length of the straight chain is $L = m\sigma$. This value of the second virial coefficient happens to be the same as the value obtained for the second virial coefficient of an infinitely long hard rod [10].

The properties of hard-chain molecules calculated from Eq. (8) can be compared with the computer simulation results of Tildesley and Streett for a hard-disphere ($m = 2$) fluid [11] and with simulation results for flexible chains made up of $m = 4$, 8, and 16 tangent hard spheres by Dickman and Hall [12]. In Fig. 4 we show the compressibility factor in terms of the reduced density of chain molecules. Excellent agreement is found between the results of theory and those of simulation for the hard-disphere fluid, $m = 2$. Good agreement is found in the case of chains of four hard spheres, $m = 4$, although the theory slightly overestimates the simulation results for

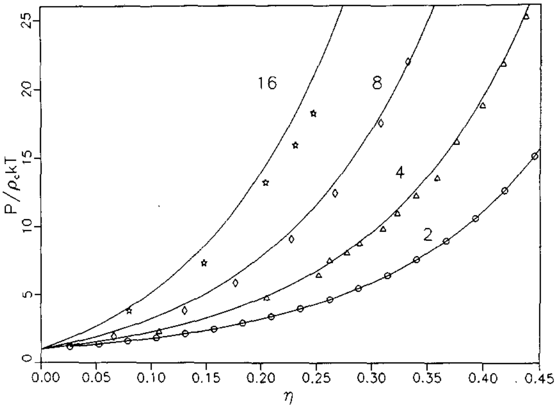

Fig. 4. The compressibility factor $P/(\rho_c kT)$ for chains of $m=2$, 4, 8, and 16 hard spheres, where ρ_c is the number density of chains. The computer simulation results of Tildesley and Streett [10] for $m=2$ and of Dickman and Hall [11] for $m=4$, 8, and 16 are represented by the data points, and the solid curve is obtained from Eq. (8).

moderate liquid densities $(0.2<\eta<0.4)$. A similar result is also found for chains of eight spheres, $m=8$, but deviations of the theoretical results from the exact simulation data are now more noticeable than for the shorter hard-sphere chains. The agreement is not as good for the chains with $m=16$, which indicates the inability of the theory to account for the steric self-hindrance of the longer chains.

In order to study the phase equilibria of associating chain molecules, mean-field and bonding contributions must be included:

$$Z = Z_{\mathrm{HC}} + Z_{\mathrm{MF}} + Z_{\mathrm{bond}} \tag{11}$$

If we assume that each sphere in the chain contributes to the mean-field energy, Eq. (3) can be used for Z_{MF}. Z_{bond} is obtained by using the first-order theory as in Section 2 (see Ref. 9 for more details). The coexistence properties of associating hard-chain fluids with one or two bonding sites have been determined using Eq. (11). In all cases the site–site bonding volumes and interaction strengths are given the values of $K^* = 4.424 \times 10^{-5}$ and $\varepsilon^*_{\mathrm{site}} = 1.0$. The reduced densities of spheres in the coexisting vapor and liquid phases are shown in Fig. 5 as a function of the reduced temperature $T^* = kT/\varepsilon_{\mathrm{MF}}$ for chains of various lengths m with one bonding site. The main effect of increasing the number of spheres in the chain is to increase the range of vapor–liquid coexistence to higher temperatures. The dashed line shown in Fig. 5 represents the locus of the critical point, and it is

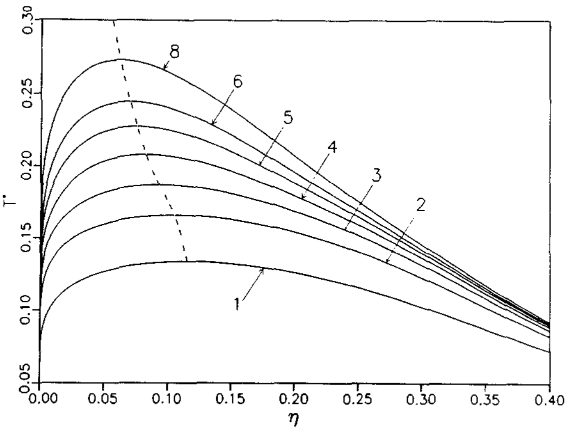

Fig. 5. Coexisting vapor and liquid densities, η, as a function of the reduced temperature, T^*, for associating chains with one square-well bonding site. As well as having bonding sites, the chain molecules have mean-field attractions to account for the dispersion forces. The curves are labeled with the corresponding values m, the number of spheres in the chain. In all cases the strength of the site–site square-well interaction is $\varepsilon^*_{\text{site}} = 1.0$, and the bonding volume is $K^* = 4.424 \times 10^{-5}$. The locus of the critical point for different values of m is shown by the dashed curve.

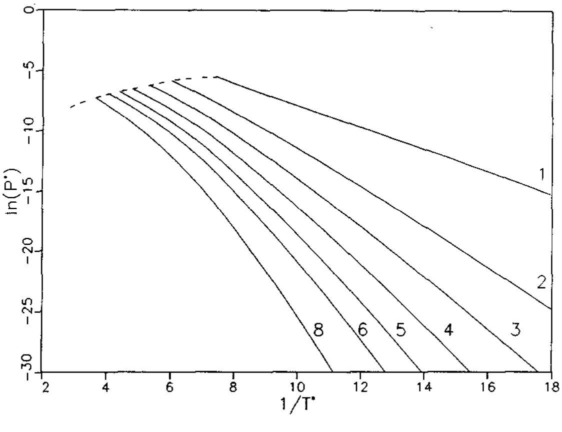

Fig. 6. The vapor–pressure curves for associating chains with one bonding site, for various sizes m. $\varepsilon^*_{\text{site}} = 1.0$ and $K^* = 4.424 \times 10^{-5}$ for all the systems. The dashed line represents the locus of critical points.

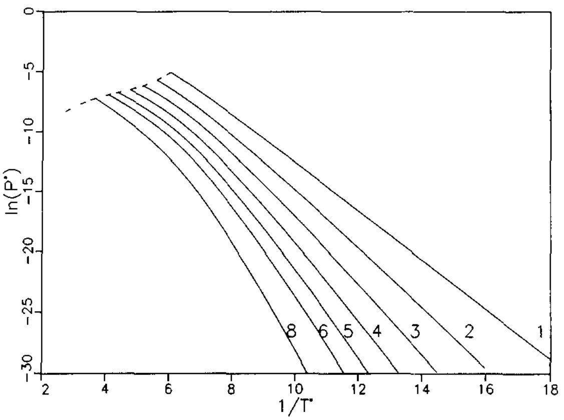

Fig. 7. The vapor–pressure curves for associating chains with two bonding sites, for various values of m. $\varepsilon^*_{\text{site}} = 1.0$ and $K^* = 4.424 \times 10^{-5}$ for all the systems.

clear that the critical density falls as the chain length increases. The vapor–pressure curves obtained for the chain fluids with one bonding site are plotted in Fig. 6; here, we show $\ln P^*$ $\{$where $P^* = P[(\pi/6)\,\sigma^3]/\varepsilon_{\text{MF}}\}$ versus $1/T^*$ for chains of various sizes m. The slopes of the curves become more negative as the chain length increases, and a distinct change in slope is found at lower temperatures in the case of the longer chains, caused by increased bonding in the liquid phase. The corresponding vapor–pressure curves obtained for chain fluids of various sizes m with two bonding sites are shown in Fig. 7. As with the one-site system (Fig. 6), the slopes of the curves become more negative with increasing chain length; the values are more negative than those obtained for corresponding curves of the one-site system. However, the effect of the molecular association decreases for larger values of m, so that the chain size becomes the dominant effect. Although the effect of bonding seems to decrease with increasing chain size, the extent of association still has an influence on the shape of the vapor–pressure curves; the curves in Figs. 6 and 7 show sharp changes in the slope at lower temperatures due to increases in the bonding, especially for the longer chains.

4. CONCLUSION

We have developed an equation of state which can take into account the effects of both molecular shape and association. Results for the reference equation of state were compared with the computer simulation data, and excellent agreement was obtained. The next phase of the research will involve the development and testing of a more sophisticated equation of state based on the equations of the present work. Furthermore, we have recently extended these equations to deal with mixtures of associating chain molecules [9] and plan to investigate the effects of association in binary and ternary mixtures of industrial interest.

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