International Journal of Thermophysics, Vol. 17, No. 1, 1996

The Theoretical Prediction of the Cricital Points of Alkanes, Perfluoroalkanes, and Their Mixtures Using Bonded Hard-Sphere (BHS) Theory[1]

A. L. Archer,[2,3] M. D. Amos,[2] G. Jackson,[2] and I. A. McLure[2]

The adequacy of the recently developed bonded hard-sphere (BHS) theory in describing the critical behavior of the homologous series of the alkanes and perfluoroalkanes is examined in this work. A simple united atom model, formed from chains of tangent hard spheres, reproduces the major experimental trends and provides good quantitative agreement for systems with two or more carbon atoms. This simple model cannot, however, reproduce the anomalous behavior of the critical pressure of the alkane series: the values of the critical pressure and temperature for methane are smaller than expected. A more sophisticated distributed-site model, which takes explicit account of the backbone and substituent atoms, reproduces this anomalous behavior. The BHS theory has also been used to predict the upper critical solution temperatures of alkane + perfluoroalkane mixtures. For most systems, the segment–segment parameters are fitted to the butane + perfluorobutane system, although in the case of mixtures containing methane, methane + perfluoromethane parameters must be used. Excellent qualitative agreement with experimental data is seen. This indicates the strength of the BHS approach as a type of group contribution method.

KEY WORDS: alkane–perfluoroalkane systems; bonded hard-sphere theory; critical behavior; phase equilibria.

1. INTRODUCTION

Alkanes and perfluoroalkanes have been extensively studied in the last 50 years over a wide range of chain lengths. Both series of homologues show a regular variation in properties, for example, the critical points, as the

---

[1] Paper presented at the Twelfth Symposium on Thermophysical Properties, June 19–24, 1994, Boulder, Colorado, U.S.A.

[2] Department of Chemistry, The University, Sheffield S3 7HF, United Kingdom.

[3] To whom correspondence should be addressed at ICI Klea, The Heath, Runcorn, Cheshire WA7 4QD, United Kingdom.

0195-928X/96/0100-0201$09.50/0 © 1996 Plenum Publishing Corporation

chain length varies, although certain anomalies are apparent. Although both alkanes and perfluoroalkanes are nonpolar species, and thus might be expected to mix almost ideally, in reality their mixtures display strikingly large positive deviations from ideality. Thus, all but one of the mixtures studied to date display limited miscibility with associated upper critical solution temperatures (UCSTs). The now-accepted explanation for this behavior rests on an unusually weak unlike molecular interaction, with a corresponding failure of the Berthelot or geometric-mean combining rule.

Although a large amount of experimental data is available for alkane + perfluoroalkane (A + PFA) systems, relatively little effort has been expended on their theoretical analysis. In the early development of the field, Scott and Hildebrand [1] used the "regular solution" or "solubility parameter" theory, which works qualitatively for most nonpolar nonelectrolyte solutions, to identify the irregularity of the thermodynamics. In 1958 Scott [2] reviewed various explanations of this anomalous behavior and concluded that none of the proposed suggestions accounted fully for the anomalous behavior of all systems investigated. Dyke et al. [3] concluded from studies of the gas–liquid critical locus that the unlike interaction is weak. Subsequent attemps at a theoretical description were, in the main, restricted to methane + perfluoromethane [4], relying heavily on the interaction weakness demonstrated by the second virial coefficients for that mixture. Abe and Flory [5] have described the upper critical solution temperature in a comprehensive fashion and a similar exercise focused on the excess properties has been carried out by Galindo and McLure [6]. Such comprehensive experimental data present alkane + perfluoroalkane mixtures as an excellent opportunity for a comprehensive and searching test of chain molecule theories. This work represents the first attempt to account for the liquid–liquid thermodynamics of A + PFA mixtures using the bonded hard-sphere (BHS) theory.

The BHS expression for the equation of state of a polyatomic hard-sphere molecule is related to that of a corresponding mixture of hard spheres with bonding sites by examining the limit of complete association. The approach has its roots in the theory of Wertheim [7], first used to determine the equation of state of homonuclear hard-sphere diatomics [8] and of homonuclear chains of m tangent hard spheres [9, 10]; the latter model is examined extensively in this work. The BHS theory, as such, was originally developed for heteronuclear diatomic molecules formed from tangentially bonded hard spheres [11]. Later it was extended to symmetrical and asymmetrical triatomic molecules [12] and to model alkane-like molecules which incorporate the identities of the backbone and substituent atoms as hard-sphere sites [13]; this type of model is examined here in order to deal with the anomalously small critical pressure of methane.

Recently, the BHS theory has been generalized to deal with ring molecules [14]. A general analytical expression for mixtures of polyatomic molecules formed from any number of hard-sphere sites is now available [15]. In these papers the BHS equation of state was found to be in excellent agreement with Monte Carlo computer simulation data for the fluid state of both the pure components and the mixtures. Although the theory cannot be used in this form to examine the effect of molecular flexibility, it can be extended to higher order to overcome these problems. [9, 16, 17].

There have only been a limited number of studies in which experimental phase equilibrium data are examined within the framework of the Wertheim and BHS theories. The theory has been shown to reproduce the data for a few selected pure compounds [18]. Radosz and co-workers have used the SAFT version of Wertheims theory for associating chains of Lennard–Jones segments to make an extensive examination of the phase equilibria of fluid mixtures and polymer solutions (for examples, see Ref. 19). As far as mixtures are concerned, the approach has been used in calculations of the phase equilibria of aqueous solutions of chain molecules [20, 21]. However, the study was a qualitative one in which simple relationships were retained for the various intermolecular parameters. The theory has not as yet been tested in a rigorous manner with experimental data for different classes of compounds. The work described in this paper represents the first of a series of studies in which the adequacy of the Wertheim and BHS theories in describing the thermodynamic properties of fluids and fluid mixtures is examined in more detail. We start by focusing on the beguiling systems containing alkanes and perfluoroalkanes.

2. THEORY

The bonded hard-sphere (BHS) approach was developed to provide an equation of state for hard-core models which are formed by bonding together hard-sphere segments of different size. The general equation of state for a multicomponent mixture of molecules formed from tangent hard spheres can be expressed in terms of the compressibility factor as [15]

$$Z^{\mathrm{BHS}}=\frac{pV}{N_m kT}=\sum_i x_i N_i^s Z^{hs}-\sum_i x_i \sum_{\text{bonds}} \left\{1+\frac{\rho}{g_{jk}^{hs}(\sigma_{jk})}\left(\frac{\partial g_{jk}^{hs}(\sigma_{jk})}{\partial \rho}\right)_{T,N}\right\} \tag{1}$$

Here ρ is the pressure, V is the volume, T is the temperature, N_m is the total number of molecules, N_i^s is the number of hard-sphere segments making up a molecule of type i, $x_i = N_i/N_m$ is the mole fraction of molecules of type i, and k is Boltzmann's constant. The first sum is over all components, i, in the mixture and the second is over the number of bonding contacts, jk, on the molecule. The expression is given in terms of the hard-sphere compressibility factor, Z^{hs}, for a corresponding reference system of unbonded hard spheres [22], and g_{jk}^{hs} is the hard-sphere pair radial distribution function for a pair of hard spheres with diameter j and k.

Simpler expressions can be obtained from Eq. (1) for more specific cases. For example, the equation of state for N_m chains formed from m tangent hard spheres of the same diameter σ is given in Ref. 10. Similar expressions for a binary mixture of chains with m_1 and m_2 hard-sphere segments can be obtained from Eq. (1). Models such as the ones described here are so-called "united atom" models of chain molecules (see Fig. 1a). United atom chain models are often too crude to reproduce some of the finer details of the behavior of real chain molecules. For example, the anomalously low critical pressure of methane compared to the other alkanes, often attributed to an "end effect," is hard to describe in terms of such theories.

An improved hard-sphere chain model with a more accurate representation of the repulsive interaction should incorporate a more explicit description of the structure of the chain, particulary the chain backbone and the substituent atoms. A model containing this provision is the "distributed-site" model in which the chain molecule is represented by a number of linked spherical sites which usually coincide with the individual atoms forming the molecule. In the case of alkanes, there is one type of sphere for the backbone chain and another type for the substituent (see Figs. 1b–d). The equation of state for this type of chain model comprising n carbon-like units has been given [13].

In order to examine fluid phase equilibria, attractive interactions must also be included. For the sake of simplicity, we use a simple van der Waals one-fluid theory to describe attractive interactions between the segments of the mixture. Of course, more realistic but complicated expressions can be used (for example, with the SAFT theory), but as we shall find, the van der Waals attractive term is sufficient to reproduce the fluid critical behavior with quantitative accuracy. However, we do find that a proper account of the repulsive interactions is crucial.

In the case of the binary mixture of chains with m_1 and m_2 chains of tangent hard spheres, the van der Waals attractive term can be written as

$$Z^{\mathrm{vdW}} = -(x_1^2 m_1^2 a_{11} + 2x_1 x_2 m_1 m_2 a_{12} + x_2^2 m_2^2 a_{22}) \frac{N_m^2}{V^2} \left(\frac{V}{N_m kT}\right) \qquad (2)$$

It is important to note that these expressions are written in terms of the number of hard-sphere segments because we are taking into account all

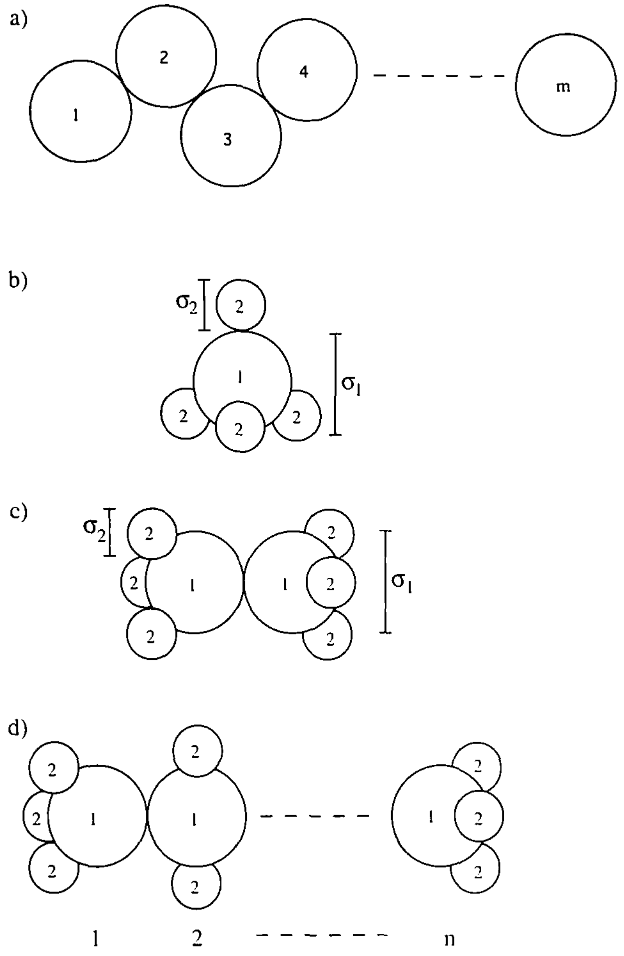

Fig. 1. The united atom model of the alkanes and perfluoroalkanes. (a) Linear chain molecules formed from m tangentially bonded hard-sphere segments of diameter σ. The distributed-site models of the alkanes and perfluoroalkanes. (b) Methane-like molecules formed from a central hard sphere of diameter σ_1 and four tetrahedrally bonded substituent hard spheres of diameter σ_2. (c) Ethane-like molecules formed from two bonded backbone hard spheres of diameter σ_1 and six tetrahedrally bonded substituent hard spheres of diameter σ_2. (d) Chains of alkane-like molecules formed from n bonded backbone hard spheres of diameter σ_1 and $2n+2$ hard spheres of diameter σ_2.

segment–segment interactions, where the segment is a united atom representation of part of the molecule. The a_{ij} parameter accounts for the segment–segment interaction between segments i and j.

In the special case of our improved distributed-site models of the pure alkanes, the attractive term can be obtained as a special case of Eq. (2), since the mole fractions of the backbone and substituent spheres are given by the values $x_1^s = n/(3n+2)$ and $x_2^s = (2n+2)/(3n+2)$, respectively. Now the a_{ij}'s correspond to segment–segment attractive interactions for the different types of sites on the molecule. The final expression for the compressibility factor is obtained by combining Eqs. (1) and (2), the repulsive attractive contributions. Details of the numerical techniques used to determine phase equilibria in our study can be found elsewhere (for example, Refs. 20 and 27).

3. RESULTS AND DISCUSSION

The BHS equation of state for homonuclear hard-sphere chain molecules has already been used with a van der Waals mean field term to describe the dependence of the critical point on the chain length of n-alkanes [23]. In order to predict the critical points, the first and second derivatives of the pressure with respect to volume must be zero. These conditions are solved numerically for a number of chain lengths m. Since the carbon–carbon bond length in the alkyl chain is approximately one-third that of the diameter of the methane molecule, a relationship between the number of carbon atoms, C, and the number of spheres in the chain, m, can be expressed as $m_1 = 1 + (C-1)/3$. Hence, the critical points for the whole of the homologous series can be mapped out. The values for the critical points of the alkane series are scaled to the critical point for butane ($m_1 = 2$) in Figs. 2a and b; the solid lines represent the BHS theory results for the united atom model and the data points represent the experimental results. This approach gives a reasonable agreement for the critical pressures and temperatures of the higher alkanes, but it is not sophisticated enough to reproduce finer details, for example, the anomalous progression in the critical pressure from methane to ethane (Fig. 2a). It is thought that this is an end effect which is not described by a simple united atom model. In the case of the perfluoroalkanes series, good agreement with the experimental critical temperatures and pressures is obtained with the empirical relation $m_2 = 1 + 0.37(C-1)$. The results for this series are scaled with the critical point of perfluorobutane ($m_2 = 2.11$) in Figs. 2c and d. Here, the BHS theory with a united-atom model (solid-line) provides a good representation of the critical behavior even for the smaller homologues. This suggests that the end effects are less pronounced in this

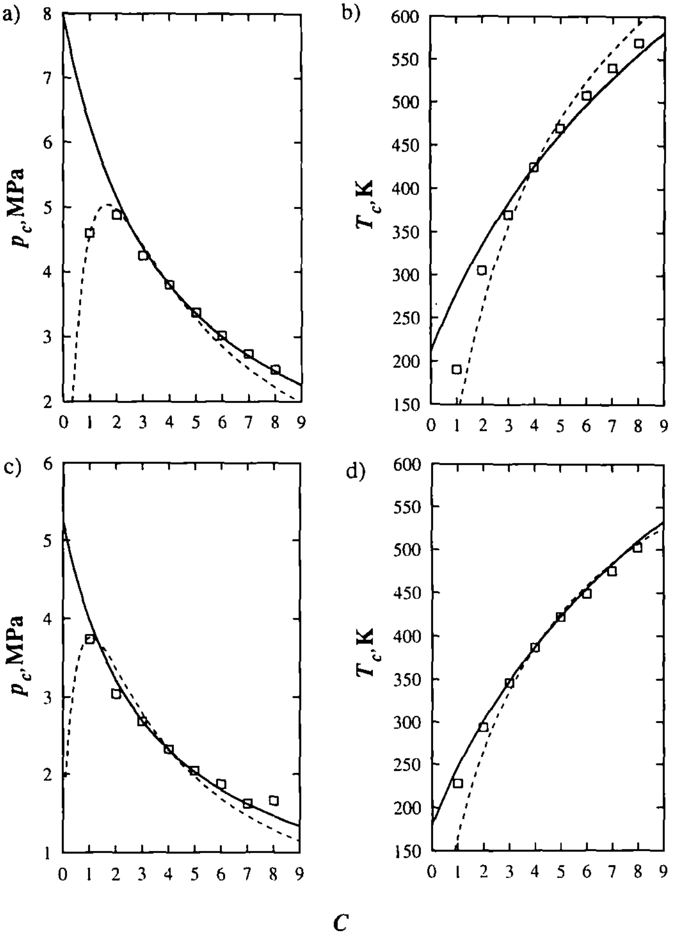

Fig. 2. (a) The critical pressures, p_c, and (b) critical temperatures, T_c, of the alkanes, and (c) the critical pressures, p_c, and (d) critical temperatures, T_c, of the perfluoroalkanes, as a function of carbon number, C. The solid curve represents the theory for the united atom model, the dashed curve represents the theory for the distributed-site model, and the data points are the experimental values [24].

system. Note that a larger segment size (0.37) is used for the perfluoroalkanes than for the alkanes.

One of the main strengths of the approach may have become apparent at this point: the properties of the whole homologous series can be obtained by fitting to a single homologue. The approach is analagous to other group-contribution methods which incorporate segment interaction parameters instead of molecular parameters.

The more sophisticated model mentioned in the previous section can be used to describe the anomaly in the behavior of the critical pressure that is seen for the alkanes. Here, the identity of the carbon backbone and the substituent atoms is retained. In the case of the alkane series the best agreement with experiment is obtained when $\sigma_2/\sigma_1 = 2$, and $a_{11} > 0$, $a_{22}/a_{11} = 0$ and $a_{12} = \sqrt{a_{11}a_{22}} = 0$. Note that we have the simple relationship $n = C$, i.e., the number of backbone spheres corresponds to the number of carbon atoms in the chain. The seemingly unphysical relationship between the outer and the inner sphere ensures that roughly the correct aspect ratio is maintained for the alkane. The theoretical results for the distributed-site model of the alkanes are shown as the dashed curves in Fig. 2; again, the critical points are scaled by that of butane. The anomaly in the critical pressure is predicted by the theory but the agreement between theory and experiment is not so good for homologues larger than hexane. The results of the theory for the distrbuted-site model of the perfluoroalkane system scaled to the critical point of perfluorobutane are represented as the dashed curves in Fig. 2 for $\sigma_2/\sigma_1 = 3$, $a_{11} > 0$, $a_{22}/a_{11} = 0.03$, and $a_{12} = \sqrt{a_{11}a_{22}}$. It seems that the important van der Waals contributions come from the backbone of the chain with nearly negligible substituent contributions. The purpose of this analysis is to illustrate qualitatively that the anomaly in the critical pressure of the alkanes can be reproduced by a more detailed model for the repulsive interactions of the molecules. In the case of the critical pressure, no value of the interaction ratio would give a better fit to the experimental data of the perfluoroalkanes. This may indicate the need for a more detailed representation of the attractive interactions than that used in the mean-field approximation, for example, the equation of state SAFT.

The equation of state for united-atom models of binary mixtures of chain molecules is used to determine the phase equilibria for model alkane + perfluoroalkane mixtures. In particular, we examine the UCST exhibited by these systems. In determining the UCST we assume that the pressure of the system is effectively zero; this is a valid approximation since the extent of liquid–liquid immiscibility is not usually very sensitive to variations in pressure.

The parameters which have to be specified for the mixtures of alkanes (component 1) and perflouroalkanes (component 2) are the sizes of the segments [$b_{11} = (\pi/6)\,\sigma_1^3$ and $b_{22} = (\pi/6)\,\sigma_2^3$], and the strengths of the a_{ij} interactions. The critical pressure and temperature of butane (3.797 MPa and 425.18 K) [24] are used to determine b_{11} and a_{11}. Similary, the critical pressure and temperature of perfluorobutane (2.323 MPa and 386.4 K)

[24] are used to determine b_{22} and a_{22}. We also need the theoretical critical points of the models for butane ($m_1 = 2$, $p^*_{1,c} = (pb_{11}^2/a_{11} = 2.679 \times 10^{-3}$, and $T^*_{1,c} = (kTb_{11})/a_{11} = 0.1439$) and perfluorobutane ($m_2 = 2.11$, $P^*_{2,c} = (pb_{22}^2)/a_{22} = 2.566 \times 10^{-3}$, and $T^*_{1,c} = (kTb_{11})/a_{11} = 0.1483$); see Refs. 10 and 19. The relationship between the parameters can be determined from $b_{22}/b_{11} = (3.797/2.323)(386.4/425.18)(2.566 \times 10^{-3}/2.679 \times 10^{-3})(0.1439/0.1483)$, $a_{22}/a_{11} = (3.797/2.323)(386.4/425.18)^2(2.566 \times 10^{-3}/2.679 \times 10^{-3})(0.1439/0.1483)^2$, and a_{12}/a_{11} is determined by fitting the theoretical UCST to that of butane + perfluorobutane (232.2 K [25]). The properties of binary mixtures containing other homologues can be obtained from the relations between the number of spheres in the chain and the number of carbon atoms obtained earlier for the pure components. Hence, the theory is essentially a group contribution theory in which the segment parameters are determined from those of butane + perfluorobutane.

We have found, however, that for mixtures containing methane the parameters had to be refitted because the united-atom model did not give a good description of methane when the parameters were fitted to butane (cf. solid curve in Fig. 2). The new parameters obtained from the critical points of methane and perfluoromethane (4.604 MPa and 190.58 K, and 3.740 MPa and 227.6 K, respectively) [24] are now $b_{22}/b_{11} = (4.604/3.740)(227.6/190.58)$, $a_{22}/a_{11} = (4.604/3.740)(227.6/1909.58)^2$, and a_{12}/a_{11} is obtained by fitting to the experimental UCST of methane + perfluoromethane (94.5 [25]). From these values of a_{ij}'s, the correction parameter ξ in the geometric-mean rule for the van der Waals cross-term can be obtained from $a_{12} = \xi(a_{11}a_{22})^{1/2}$. A value of $\xi = 0.909$ is obtained for both methane + perfluoromethane and butane + perfluorobutane. This can be compared with the value of 0.93 given by Hildebrand et al. [26] for methane + perfluoromethane.

To study different A + PFA systems, only the chain lengths of the two components, which are related to the number of carbon atoms, must be specified. The mixtures without methane are described using the butane + perfluorobutane parameters, and mixtures containing methane are described using the methane + perfluoromethane parameters. The calculated UCSTs for a number of binary A + PFA mixture are shown in Table I, along with the corresponding experimental value, where available [25]. The agreement is surprisingly good for all of the mixtures studied, the difference is generally no more than 7% from the experimental value. It must be remembered that only one mixture is being used to obtain the interaction parameters; the UCSTs of the other mixtures are obtained from these values. Almost all of the mixtures studied exhibit type II phase behavior, as classified by van Konynenburg and Scott [27]. The model predicts the trend to type III behavior when the alkane becomes significantly longer than the perfluoroalkane—seen experimentally by Wirths and Schneider [28]. To summarize we have shown that the BHS theory for a simple united-atom model of alkanes and perfluoroalkanes can be used to predict the trend in the critical point for each homologous series. Since the segment–segment interactions have to be specified in the theory, it enables the properties of one homologue to be obtained from another. The united-atom model does not, however, describe the anomaly seen in the critical pressures of the alkanes; this behavior can be described by an improved distributed-site model, which takes into acount the explicit molecular structure. The UCSTs of A + PFA mixtures can also be predicted with great succes using united-atom models.

Table I. The UCSTs of A + PFA Mixtures Where HC and FC Represent the Alkane and Perfluoroalkane with Carbon Number C

	H1	H2	H3	H4	H5	H6	H7	H8
F1	95[a]	161[b]						
	95[c]	150[c]						
F2	106[a]	172[b]	193[b]	212[b]	230[b]	250[b]	272[b]	
		157[d]	190[c]					
F3	116[a]	182[b]	204[b]	222[b]	239[b]	257[b]	272[b]	289[b]
	127[c]	166[c]	196[c]	226[c]	251[c]	276[c]		336[c]
F4		191[b]	213[b]	232[b]	249[b]	266[b]	281[b]	295[b]
			204[c]	232[c]		281[c]	303[c]	
F5		198[b]	221[b]	241[b]	258[b]	276[b]	290[b]	304[b]
					266[c]	288[c]		
F6		204[b]	228[b]	248[b]	266[b]	283[b]	298[b]	313[b]
					273[c]	296[c]	316[c]	335[c]
F7		210[b]	234[b]	255[b]	273[b]	292[b]	306[b]	320[b]
					282[c]	303[c]	323[c]	343[c]
F8		214[b]	239[b]	261[b]	280[b]	297[b]	313[b]	328[b]
				255[e]	288[e]	299[e]	320[e]	349[e]

[a] Theoretical values with parameters fitted to methane + perfluoromethane.

[b] Theoretical values with parameters fitted to butane + perfluorobutane.

[c] Experimental values from Ref. 25.

[d] In practice, no liquid–liquid immiscibility is seen for the ethane + perfluoroethane system. However, an estimated metastable liquid–liquid curve has been calculated by Gilmour et al. [25].

[e] Experimental values from Ref. 29.

REFERENCES

1. J. H. Hildebrand and R. L. Scott, *Solubility of Nonelectrolytes*, 3rd ed. (Reinhold, New York, 1950).
2. R. L. Scott, *J. Phys. Chem.* **62**:136 (1958).
3. D. E. L. Dyke, J. S. Rowlinson, and R. Thacker, *Trans. Faraday Soc.* **55**:903 (1959).
4. D. R. Douslin, R. H. Harrison, and R. T. Moore, *J. Phys. Chem.* **71**:3477 (1967); E. M. Dantzler Siebert and C. M. Knobler, *J. Phys. Chem.* **75**:3863 (1971).
5. A. Abe and P. J. Flory, *J. Am. Chem. Soc.* **88**:2887 (1966).
6. A. Galindo and I. A. McLure, in preparation (1994).
7. M. S. Wertheim, *J. Stat. Phys.* **35**:19 (1984); *J. Stat. Phys.* **35**:35 (1984); *J. Stat. Phys* **42**:459 (1986); *J. Stat. Phys.* **42**:477 (1986).
8. M. S. Wertheim, *J. Chem. Phys.* **85**:2929 (1986).
9. M. S. Wertheim, *J. Chem. Phys.* **87**:7323 (1987).
10. W. G. Chapman, G. Jackson, and K. E. Gubbins, *Mol. Phys.* **65**:1057 (1988).
11. A. L. Archer and G. Jackson, *Mol. Phys.* **73**:881 (1991).
12. M. D. Amos and G. Jackson, *Mol. Phys.* **74**:191 (1991).
13. R. P. Sear, M. D. Amos, and G. Jackson, *Mol. Phys.* **80**:777 (1993).
14. R. P. Sear and G. Jackson, *Mol. Phys.* **81**:801 (1994).
15. M. D. Amos and G. Jackson, *J. Chem. Phys.* **96**:4604 (1992).
16. S. Phan, E. Keirlik, M. L. Rosinberg, H. Yu, and G. Stell, *J. Chem. Phys.* **99**:5326 (1993).
17. E. Müller and K. E. Gubbins, *Mol. Phys.* **80**:957 (1993).
18. W. G. Chapman, K. E. Gubbins, G. Jackson, and M. Radosz, *Ind. Eng. Chem. Res.* **29**:1709 (1990).
19. C. J. Gregg, F. P. Stein, and M. Radosz, *J. Phys. Chem.* **98**:10634 (1994); J. M. U. Yu, S. H. Huang, and M. Radosz, *Fluid Phase Equil.* **93**:353 (1994); C. J. Gregg, F. P. Stein, S. J. Chen, and M. Radosz, *Ind. Eng. Chem. Res.* **32**:1442 (1993); S. H. Huang and M. Radosz, *Ind. Eng. Chem. Res.* **30**:1994 (1991).
20. D. G. Green and G. Jackson, *J. Chem. Soc. Faraday Trans.* **88**:1395 (1992).
21. D. G. Green and G. Jackson, *J. Chem. Phys.* **97**:8672 (1992).
22. T. Boublik, *J. Chem. Phys.* **53**:471 (1970).
23. G. Jackson and K. E. Gubbins, *Pure Appl. Chem.* **61**:1021 (1990).
24. D. Ambrose, *Vapour-Liquid Critical Properties*, Report Chem 107 (National Physical Laboratory, London, 1980). Also supplement of same name by same author (University College, London, 1983).
25. J. B. Gilmour, J. O. Zwicker, J. Katz, and R. L. Scott, *J. Phys. Chem.* **71**:3259 (1967); C. P. Hicks, R. L. Hurle, L. S. Toczylkin, and C. L. Young, *Aust. J. Chem.* **31**:19 (1978).
26. J. H. Hildebrand, J. M. Prausnitz, and R. L. Scott, *Regular and Related Solutions* (Reinhold, New York, 1970).
27. P. H. van Konynenburg and R. L. Scott, *Philos. Trans. R. Soc.* **298**:495 (1980).
28. M. Wirths and G. M. Schneider, *Fluid Phase Equil.* **21**:257 (1985).
29. B. Edmonds, Ph.D. thesis (University of Sheffield, 1972).