

## Thermodynamic Regularities for Associating Fluids from Statistical Associating Fluid Theory Equation of State

A. Maghari\* and Z. Safaei

Department of Physical Chemistry, University College of Science, University of Tehran, Tehran, Iran

(Received 20 September 2006, Accepted 18 January 2007)

In this work, we used a statistical associating fluid theory to analyze two important thermodynamic regularities for some associating fluids, including water, methanol and ethanol. The studied regularities included: (i) the common bulk modulus point on the isotherms of the reduced bulk modulus versus reduced density, (ii) near linearity of the reduced isothermal bulk modulus as a function of reduced pressure. In this work, we also reported the influence of the molecular size and interaction strength on the bulk modulus point.

**Keywords:** Equation of state, Isothermal bulk modulus, Statistical associating fluid theory, Tai-Murnaghan, Thermodynamic regularities

---

### INTRODUCTION

The thermodynamic behaviors of liquids and dense fluids are by far the most difficult to understand, due to the complexity of molecular interactions. They do show, however, a number of simple regularities, some of which have been recently studied for simple dense fluids [1,2]. Based on some important regularities, several van der Waals-type equations of state were tested in our earlier works for their ability to predict the regularities in simple dense fluids.

In contrast to non-polar and simple fluids, which have structures that depend primarily on short-range repulsive interactions, in strongly associating fluids, the strong attractive interactions (i.e. hydrogen bonding) between molecules result in the formation of molecular clusters that have considerable effect on the thermodynamic and structural properties of the species.

Based on thermodynamic perturbation theory of Wertheim

[3-6], statistical associating fluid theory (SAFT) has been proposed by Chapman *et al.* [7,8] and Huang and Radosz [9] and widely used in the past decade from simple chain to polydisperse fluids. The SAFT equation of state (EoS) has a more appropriate reference than the EoS of the van der Waals class, since it incorporates the chain length, molecular association and other interactions such as long-range dipolar forces and dispersions.

In this paper, we show that, unlike the cubic van der Waals-type EoS, a precise statistical associating fluid theory describes the most important regularities. Since the SAFT EoS has a theoretical basis, analysis of the regularities in terms of molecular properties is possible. Two of the best known regularities, studied in this work, are the following:

(1) The common bulk modulus intersection point, proposed by Huang and O'Connell [10] as a regularity. In their studies, it has been observed that the bulk modulus  $B_T$ , which is the reciprocal of isothermal compressibility  $\kappa_T$ , as a function of density at different temperatures approach and intersect each other at a characteristic density. The location of

---

\*Corresponding author. E-mail: maghari@khayam.ut.ac.ir

the common modulus point depends on the particular liquid. The analysis of EoS models in terms of derived properties such as  $\kappa_T$  or  $B_T$  has interesting advantages, since these properties are related to the first derivatives of the  $(p, V, T)$  EoS, and can be accurately measured over wide ranges of pressure and temperature by different experimental techniques.

(2) Near linearity of the isothermal bulk modulus of a liquid or supercritical fluid as a function of pressure. This regularity is now called the Tait-Murnaghan regularity [11].

In this work, we use the SAFT EoS to predict the two abovementioned regularities for three associating fluids, including water, methanol and ethanol. The influence of the molecular size and interaction strength on the bulk modulus point is reported.

## EQUATION OF STATE

Within the statistical associating fluid theory framework, the residual Helmholtz energy for a fluid of associating chain molecules is written as the sum of the separate contributions to the energy:

$$A^{\text{res}} \equiv A - A^{\text{ideal}} = A^{\text{seg}} + A^{\text{chain}} + A^{\text{dd}} + A^{\text{assoc}} \quad (1)$$

where  $A$  and  $A^{\text{ideal}}$  are the total Helmholtz energy and the ideal gas Helmholtz energy at the same temperature and density,  $A^{\text{seg}}$  is the Helmholtz energy due to segment-segment interactions considered to be the reference term,  $A^{\text{chain}}$  is the contribution due to the formation of a chain of  $m$  monomers,  $A^{\text{dd}}$  is the Helmholtz energy due to the dipole-dipole interaction and possible induction interactions, and  $A^{\text{assoc}}$  is the incremental Helmholtz energy due to association.

In this work, the two best known regularities for associating fluids have been studied. They are the common bulk modulus point and the linearity of the reduced isothermal bulk modulus as a function of reduced pressure, predicted using the Lennard-Jones (LJ) SAFT EoS of Müller and Gubbins [12] and Kraska and Gubbins [13].

### Segment Term

In the LJ-SAFT equation, the segment term can be given as

$$A^{\text{seg}} = m \left[ A^{\text{hs}} + \exp(-\gamma \rho^{*2}) \rho^* T \Delta B_{2,\text{hBH}} + \sum_{i,j} C_{ij} T^{i/2} \rho^{*j} \right] \quad (2)$$

where

$$A^{\text{hs}} = Nk_B T \left[ \frac{5}{3} \ln(1-\eta) + \frac{\eta(34-33\eta+4\eta^2)}{6(1-\eta)^2} \right] \quad (3)$$

$$\Delta B_{2,\text{hBH}} = \sum_{i=-7}^0 C_i T^{i/2} \quad (4)$$

$$\rho^* = \frac{6mV^{00}}{\pi} \rho \quad (5)$$

$$\eta = \frac{\pi}{6} \rho^* \sigma_{\text{BH}}^3 \quad (6)$$

$$\sigma_{\text{BH}} = \sum_{k=-2}^1 D_k T^{k/2} + D_{\ln} \ln T \quad (7)$$

where  $m$  is segment number and  $\rho$  is molar density.

### Chain Term

The chain contribution in the LJ-SAFT model is described by Johnston *et al.* [14] as:

$$A^{\text{chain,LJ}} = Nk_B T (1-m) \ln [g^{\text{LJ}}(\sigma)] \quad (8)$$

where  $g^{\text{LJ}}(\sigma)$  is the LJ radial distribution function at  $r = \sigma$ .

### Dipole-Dipole Term

The effects of direct electrostatic interactions between molecules can be expressed by multi-polar expansion. For associating fluids, the leading term of the point dipole-point dipole interaction is only considered and is given by:

$$A^{\text{dd}} = Nk_B \tilde{T} A_2 \left( \frac{1}{1 - (A_3/A_2)} \right) \quad (9)$$

where

$$A_2 \equiv -\frac{2\pi}{3} \frac{\rho^* \mu^{*4}}{T^*} J^{(6)} \quad (10)$$

## Thermodynamic Regularities for Associating Fluids

$$A_3 \equiv \frac{32\pi^3}{135} \sqrt{\frac{14\pi}{5}} \frac{\rho^{*2} \mu^{*6}}{T^{*2}} K_{222}^{333} \quad (11)$$

$$\tilde{T} \equiv \frac{k_B T}{\varepsilon} \quad (12)$$

$$\mu^* \equiv \frac{1}{(4\pi\varepsilon_0)^{1/2}} \frac{\mu}{\sqrt{m\varepsilon\sigma^3}} \quad (13)$$

where  $\varepsilon$  is the potential well-depth parameter and  $\mu$  is the dipole moment of the molecule. The coefficients  $J^{(6)}$  and  $K_{222}^{333}$  are integrals over two-body and three-body correlation functions for the LJ fluids [15,16], and  $\varepsilon_0 = 8.9 \times 10^{-12} \text{C}^2 \text{N}^{-1} \text{m}^{-2}$  is the electric permittivity.

### Association Term

The association contribution to the Helmholtz function is based on the first-order thermodynamic perturbation theory of Wertheim [3-6]. The expressions for the free energy due to association is given by

$$A^{\text{assoc}} = Nk_B T \left\{ \frac{M}{2} + \sum_{a=1}^M \left( \ln X_a - \frac{X_a}{2} \right) \right\} \quad (14)$$

where  $X_a$  is the fraction of molecules not bonded at site  $a$ , and  $M$  is the number of site per molecule, which is equal to 4 for water and 2 for methanol. The monomer fraction is related to the association strength  $\Delta$  as follows:

$$X_a = \frac{1}{1 + N \sum_b \rho X_b A_{ab}} \quad (15)$$

The association strength is an integral over the radial

distribution function of the reference fluid multiplied by the Mayer function of the association potential, which was simplified by Gubbins *et al.* [12,17,18]:

$$\Delta = 4\pi K_{\text{assoc}} \left[ \exp\left(\frac{\varepsilon_{\text{assoc}}}{k_B T}\right) - 1 \right] I(\rho^*, T^*) \quad (16)$$

where  $K_{\text{assoc}}$  is an adjustable parameter. The integral  $I(\rho^*, T^*)$  has been evaluated numerically using the accurate values for the LJ radial distribution function obtained from molecular dynamics simulations and fitted as a function of reduced temperature and reduced density [12]:

$$I(\rho^*, T^*) = \frac{1}{3.84 \times 10^4} \sum_{k=1}^4 \sum_{l=1}^4 A_{kl} \rho^{*k} T^{*l} \quad \rho^* \leq 1.25; \quad 0.7 \leq T^* \leq 6.0 \quad (17)$$

The parameters of LJ-SAFT can be obtained by simultaneously fitting the experimental saturated vapor pressures and liquid densities. The regressed parameters for associating fluids [12,13] are shown in Table 1.

## RESULTS AND DISCUSSION

In our previous paper [1], we evaluated 10 van der Waals-type EoSs for their ability to predict the most important regularities. We observed that the predictive ability of isothermal bulk modulus of non-polar fluids obtained from the cubic EoSs are poor, especially at higher densities. In our second paper [2], we showed that, unlike the cubic van der Waals-type EoS, a precise statistical mechanical EoS, called Deiters EoS, describes the common intersection point of non-polar and weakly polar fluids. In this work, we have

**Table 1.** Parameters of SAFT Equation for Associating Fluids

Substance	$m$	$K_{\text{assoc}}$	$\varepsilon_{\text{assoc}}/k_B$ (K)	$v^{00}$ (ml/mol)	$\varepsilon/k_B$ (K)	$\mu$ (D)
Water	1.00	67.003	1415.32	10.4877	244.0111	2.32
Methanol	1.5862	430.591	2468.99	13.2680	121.8660	1.70
Ethanol	1.4527	58.785	3369.04	19.0642	196.8021	1.73

investigated the performance of a new statistical mechanical EoS, called the SAFT EoS, for the prediction of the two most important regularities of some associating (strongly polar) fluids.

### Common Bulk Modulus Point

The reduced bulk modulus  $B_T$ , which is a mechanical property, can be written as

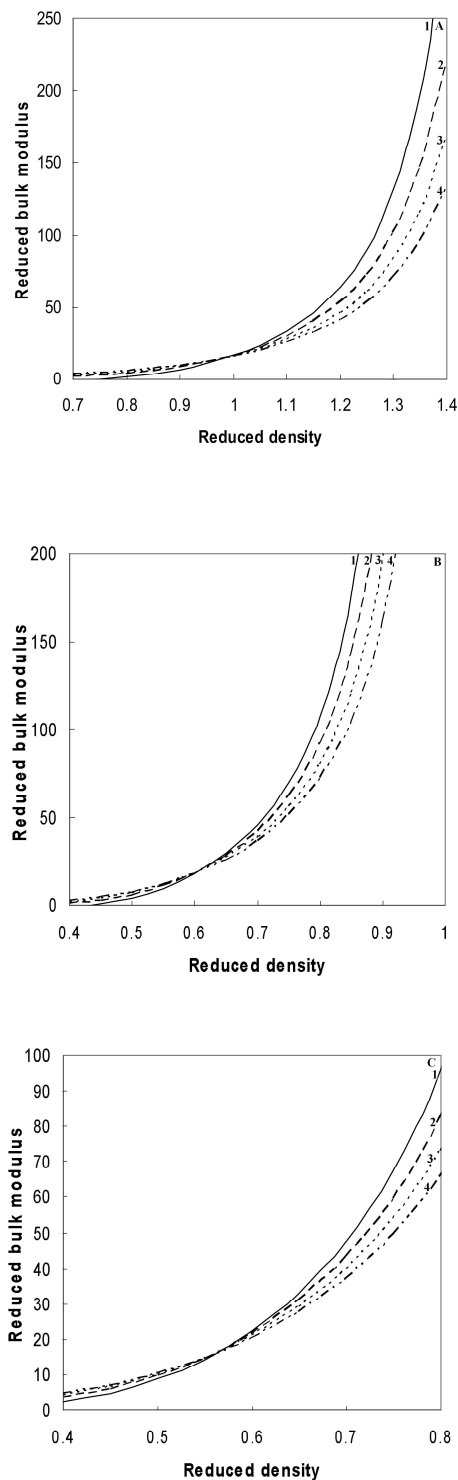
$$B_T = \frac{1}{T^*} \left( \frac{\partial p^*}{\partial \rho^*} \right)_{T^*} \quad (18)$$

where  $p^* \equiv P\sigma^3/\varepsilon$ . Experimental data show that  $B_T$  increases with increasing density at constant temperature. The isotherms of  $B_T(\rho)$  intersect at high densities for many liquids, a characteristic feature described by Huang and O'Connell [10], called the common bulk modulus point. The value of  $B_T$  is independent of temperature at this density, i.e.

$$\left( \frac{\partial B_T}{\partial T^*} \right)_{\rho_0^*} = 0 \quad (19)$$

and may correspond to either a minimum or a maximum in the  $B_T(T^*)$  isochors, where  $\rho_0^*$  is the reduced density of the fluid at the common bulk modulus point. This regularity usually lies in the liquid region and the location of the common modulus point, of course, depends on the particular liquid.

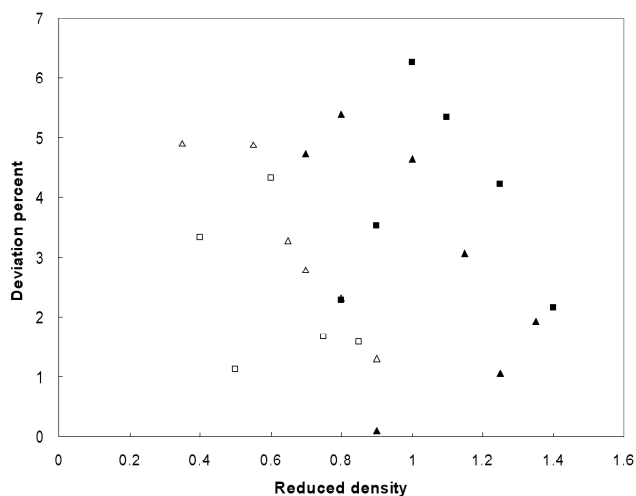
In general, the condition  $(\partial B_T / \partial T)_{\rho_0^*} = 0$  always occurs within a relatively narrow range of reduced densities. The crossover of the  $B_T(\rho)$  isotherms seems to be a general property of liquids. The results for the three associating fluids are shown in Fig. 1. As shown in our previous papers [1,2], most of the cubic van der Waals-type EoS do not show a common intersection point. However, in this work we show that the SAFT EoS predicts a nearly common modulus point for associating fluids, consistent with the empirical findings of Huang and O'Connell. The predicted common intersection points  $\rho_0^*$  for the selected substances in this work are given in Table 2. Figure 2 shows the departures of the experimental bulk modulus of water and methanol, obtained from the heat capacities and speed of sound data taken from the NIST Chemistry WebBook [19] of correlated data from the



**Fig. 1.** Isothermal bulk modulus as a function of reduced density for water (A), methanol (B) and ethanol (C).

**Table 2.** Predicted Common Intersection Point

Substance	$\rho_0^*$	$B_T(\rho_0^*)$
Water	0.995	16.2
Methanol	0.542	43.5
Ethanol	0.567	16.3


**Fig. 2.** Deviation plot of the experimental bulk-modulus of water and methanol from the calculated results. The experimental data taken from NIST WebBook [19].

calculated results, which are seen to be consistent with the estimated experimental errors. As far as the authors aware there are no data for ethanol in the literature to compare to our results. In our present work, the experimental isothermal bulk modulus of fluids is determined from the heat capacity ratio and speed of sound data described in the following manner.

The propagation of sonic waves is nearly isentropic, so by using Eq. (18) we can calculate the isentropic sound velocity  $v_s$  for real systems as

$$v_s = \left[ \frac{\gamma RT}{M} \left( \frac{\partial P_r}{\partial \rho_r} \right)_{T_r} \right]^{1/2} \quad (20)$$

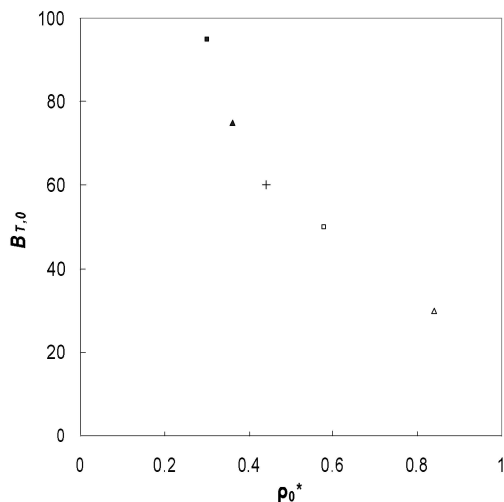
in which  $R$  is the universal gas constant,  $M$  is the molecular

weight and  $\gamma$  is the heat capacity ratio  $\gamma \equiv C_p/C_v$ . Therefore, the experimental values of the isothermal bulk modulus can be obtained from the experimental data of the speed of sound and the heat capacity ratio of the system as

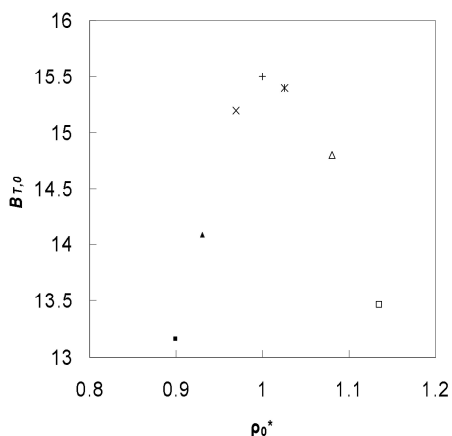
$$B_T = \frac{M}{\gamma RT} v_s^2 \quad (21)$$

In fact, the bulk modulus, as well as the sound velocity, is a second order derivative property that is most sensitive to deviations and generally represented as a severe consistency test for EoSs, since it involves the partial derivative of pressure with respect to density, and to achieve this the EoSs must describe with great accuracy the  $p(\rho, T)$ . As seen from Fig. 1, the SAFT EoS yields good representation of the common bulk modulus intersection point for associating fluids. A general observation is that  $B_r(\rho, T)$  always increases with density at constant temperature. As shown in Fig. 2, the agreement observed between the SAFT predictions and data taken from a correlation to experimental data of NIST [19] at two different reduced temperatures are good for isothermal bulk modulus. Mean AAD% for water and methanol are 2.9 and 2.1%, respectively.

In order to analyze the general observations described in the previous section, we shall start examining the influence of the molecular parameters to the common bulk modulus intersection point. For this purpose, we consider some arbitrary systems with the same SAFT EoS, but using four different sets of molecular parameters, i.e. segment number  $m$  and reduced dipole moment  $\mu^*$ . As seen in Fig. 3, the intersection point moves towards lower  $\rho_0^*$  and higher  $B_{T,0}$  as the segment number  $m$  is increased. Figure 4 also displays the effect of the molecular dipole moment on the common intersection point. Here, the intersection point moves toward the larger  $\rho_0^*$  as the reduced dipole moment  $\mu^*$  is increased. Moreover, the bulk modulus at the intersection point  $B_{T,0}$  increased with increasing  $\mu^*$  when  $\rho_0^* < 1$ , and decreased when  $\rho_0^* > 1$ . Note that for water and alkanols with a low carbon number (like CH<sub>3</sub>OH) the dipole interaction is expected to be very important. We have also observed that the associating parameters,  $K_{assoc}$  and  $\varepsilon_{assoc}$ , do not have any significant effects on the location of the common intersection point.



**Fig. 3.** Effect of segment number on the location of intersection point: ( $\Delta$ )  $m = 1.0$ , ( $\square$ )  $m = 1.5$ , (+)  $m = 2.0$ , ( $\blacktriangle$ )  $m = 2.5$ , ( $\blacksquare$ )  $m = 3.0$ .



**Fig. 4.** Effect of molecular dipole interaction  $\mu^*$  on the location of intersection point: ( $\blacksquare$ )  $\mu^* = 1.0$ ; ( $\blacktriangle$ )  $\mu^* = 1.5$ , ( $\times$ )  $\mu^* = 2.0$ , (+)  $\mu^* = 2.5$ , (\*)  $\mu^* = 3.0$ , ( $\Delta$ )  $\mu^* = 4.0$ , ( $\square$ )  $\mu^* = 5.0$ .

These results point to the interesting conclusion that the condition  $(\partial B_T / \partial T)_{\rho_0^*} = 0$  may correspond to either a minimum or a maximum in the  $B_T(T^*)$  isochors. It can easily be shown that this condition equals the maxima or minima in  $\rho(\partial Z / \partial T)_\rho$ , where  $Z$  is the compressibility factor. Within the physical concept of intermolecular forces, the compressibility

factor is written as a sum of the separate contributions of attraction  $Z_{att}$  and repulsion  $Z_{rep}$ . The common bulk modulus intersection point occurs where

$$\frac{\partial}{\partial \rho} \left[ \rho \left( \frac{\partial Z_{att}}{\partial T} \right) \right] = \frac{\partial}{\partial \rho} \left[ \rho \left( \frac{\partial Z_{rep}}{\partial T} \right) \right]$$

### Linearity of $B_T$ vs. Pressure

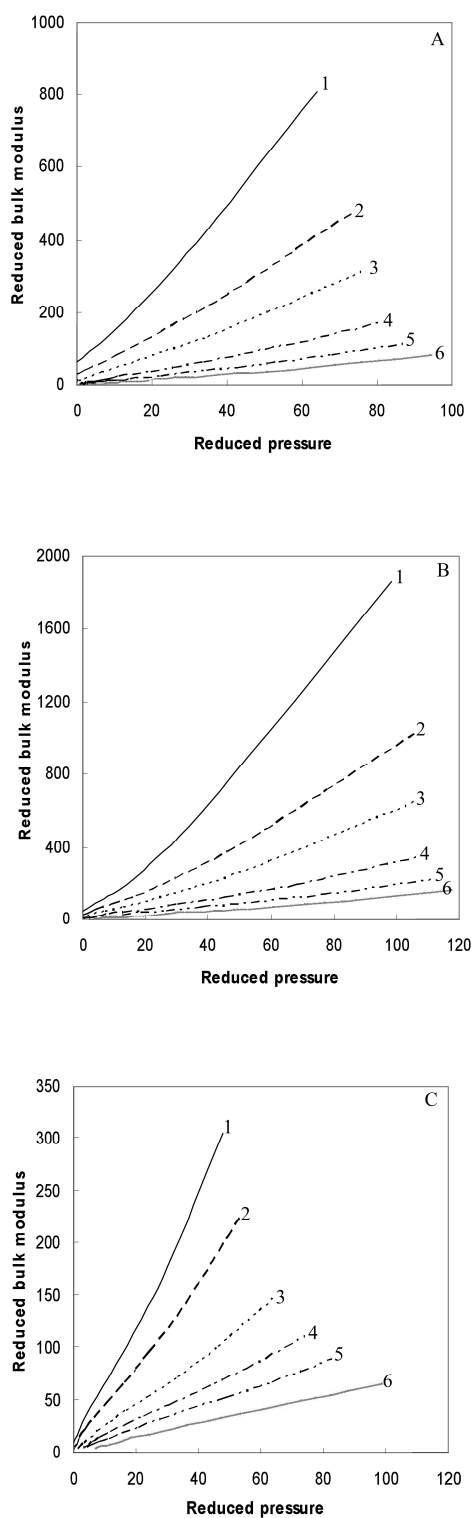
The reduced bulk modulus of a dense fluid has been empirically found to be linear in the reduced pressure for each isotherm, i.e.

$$B_T = B_0 + B'_0 p^* \quad (22)$$

where  $B_0$  and  $B'_0$  are temperature-dependent parameters. Such linearity is known as the Tait-Murnaghan regularity. This regularity is satisfactory for a number of successful empirical equations of state, such as Peng-Robinson, Soave-Redlich-Kwong, modified Patel-Teja and Deiters equations of state for normal dense fluids [1,2]. It is also interesting to examine the behavior of the pressure dependence of the isothermal bulk modulus of associating dense fluids when comparing non-polar and polar fluids. Figure 5 shows the calculated isothermal reduced bulk modulus  $B_T$  as a function of reduced pressure for six reduced temperatures. As shown, at higher temperatures and pressures an approximate linear behavior of the Tait-Murnaghan regularity is obtained for all selected substances.

## CONCLUSIONS

We have analyzed the general behavior of the most important thermodynamic regularities: the common intersection point of the bulk modulus and the Tait-Murnaghan regularities for some important associating fluids. The regularity of the isothermal bulk modulus as a function of reduced density retains its common intersection even in compressed liquid. The Tait-Murnaghan regularity of the isothermal bulk modulus as a function of reduced pressure exists for both subcritical and supercritical fluids over a wide pressure range. We show that the SAFT EoS predicts a nearly common modulus point for associating fluids. Our results show that the SAFT EoS can also be used to make good



**Fig. 5.** Isothermal bulk modulus as a function of reduced pressure for water (A), methanol (B) and ethanol (C).

predictions of the Tait-Murnaghan regularity as well as the common intersection points for all selected substances.

## ACKNOWLEDGEMENTS

Financial support received from the University of Tehran Research Council is greatly appreciated.

## REFERENCES

- [1] A. Maghari, L.H. Shahri, *Fluid Phase Equilib.* 206 (2003) 287.
- [2] A. Maghari, N. Tahmasbi, *Int. J. Thermophys.* 25 (2005) 205.
- [3] M.S. Wertheim, *J. Stat. Phys.* 35 (1984) 19.
- [4] M.S. Wertheim, *J. Stat. Phys.* 35 (1984) 35.
- [5] M.S. Wertheim, *J. Stat. Phys.* 42 (1984) 459.
- [6] M.S. Wertheim, *J. Stat. Phys.* 42 (1984) 477.
- [7] W.G. Chapman, K.E. Gubbins, G. Jackson, M. Radosz, *Fluid Phase Equilib.* 52 (1989) 31.
- [8] W.G. Chapman, K.E. Gubbins, G. Jackson, M. Radosz, *Ind. Eng. Chem. Res.* 29 (1990) 1709.
- [9] S.H. Huang, M. Radosz, *Ind. Eng. Chem. Res.* 29 (1990) 2284.
- [10] Y.H. Huang, J.P. O'Connell, *Fluid Phase Equilib.* 37 (1987) 75.
- [11] J.R. Macdonald, *Rev. Mod. Phys.* 40 (1969) 316.
- [12] E.A. Müller, K.E. Gubbins, *Ind. Eng. Chem. Res.* 34 (1995) 3662.
- [13] T. Kraska, K.E. Gubbins, *Ind. Eng. Chem. Res.* 35 (1996) 4727.
- [14] J.K. Johnson, E.A. Müller, K.E. Gubbins, *J. Chem. Phys.* 98 (1994) 6413.
- [15] C.H. Twu, K.E. Gubbins, *Chem. Eng. Sci.* 33 (1978) 863.
- [16] C.H. Twu, K.E. Gubbins, *Chem. Eng. Sci.* 33 (1978) 879.
- [17] J.K. Johnson, K.E. Gubbins, *Mol. Phys.* 77 (1992) 1033.
- [18] J.M. Walsh, E.A. Muller, K.E. Gubbins, *Mol. Phys.* 80 (1993) 65.
- [19] NIST Chemistry Webbook, NIST Standard Reference Database Number 69, National Institute of Standards and Technology (<http://webbook.nist.gov>).