

Common Intersection Point Independent of Mole Fraction: A New Regularity

E. K. Goharshadi^{1, 3} and A. Boushehri¹

Received May 8, 1997

A new regularity has been found for compressed liquid mixtures, namely, a common intersection point for the isotherms of the reduced bulk modulus of a compressed liquid mixture as a function of composition. The regularity holds over a specific range of densities from a particular liquid mixture. The regularity has been tested for a LJ (12,6) mixture, Ar + Kr, Kr + Xe, and CO₂ + C₂H₆, based on equations of state derived from statistical mechanics and it is valid close to within experimental accuracy.

KEY WORDS: bulk modulus; equation of state; liquid mixture.

1. INTRODUCTION

Liquids and dense fluids are usually considered to be complicated on a molecular scale. However, they show a number of simple rarities. Seven of the better-known ones are the following.

- (1) Near-linearity of the pressure versus the temperature at constant density, over the entire range from the perfect gas to the compressed liquid [1].
- (2) Near-linearity of $\log P$ versus $1/T$ over the entire liquid from the triple point to the critical point [2].
- (3) Near-linearity of the mean density of a saturated liquid and its equilibrium vapor as a function of temperature. This is the so-called "law of rectilinear diameter" [3].
- (4) Near-linearity of the bulk modulus (reciprocal compressibility) of a liquid as a function of pressure. This regularity, first noticed by

¹ Department of Chemistry, Shiraz University, Shiraz 71454, Iran.

² Present address: Department of Chemistry, Ferdowsi University, Masshad 91384, Iran.

³ To whom correspondence should be addressed.

Tait over 100 years ago, is the basis for a number of successful empirical equations of state for liquids [4–6].

- (5) Linearity of the zero contour and its correlation with the line of rectilinear diameter. The zero contour is the locus of T versus $1/V$ points at which the compression factor, $Z = PV/nRT$, is unity [7, 8], where V , n , and R are the volume, number of moles, and gas constant, respectively. The zero line resides in the supercritical region, whereas the line of rectilinear diameters of course lies in the subcritical region.
- (6) The common bulk modulus point, i.e., all liquid isotherms of the reduced bulk modulus as a function of the molar volume intersect at essentially a single point [9–11].
- (7) Linearity of $(Z - 1)V^2$ versus ρ^2 , where $\rho = 1/V$ is the molar density for both compressed liquids and dense supercritical fluids [12].

The purpose of this paper is to point out an additional regularity for compressed liquid mixtures. This regularity is a common intersection point for the isotherms of the reduced bulk modulus as a function of composition. The regularity holds over a specific range of densities for the particular liquid mixture, and of course, the location of the common modulus point depends on the special liquid mixture.

The regularity has been tested for a LJ(12,6) mixture and for real fluid mixtures based on equations of state derived from statistical mechanics. The real fluid mixtures are Ar + Kr, Kr + Xe, and $\text{CO}_2 + \text{C}_2\text{H}_6$. Among these mixtures, $\text{CO}_2 + \text{C}_2\text{H}_6$ has industrial importance for the processing of liquefied natural gas (LNG), because some natural gas contains an appreciable amount of CO_2 which must be separated before (or during) liquefaction to avoid its freezing at LNG temperatures. In addition, this interesting system is also suitable for study by statistical-perturbation theory, because both CO_2 and C_2H_6 have relatively simple molecular shapes. Carbon dioxide has a large quadrupole moment, whereas ethane has only a relatively small one, making this mixture valuable for testing the perturbation theory.

2. THEORETICAL FORMULATIONS

The statistical-mechanical equation of state for liquid LJ mixtures has the following form [13]:

$$P/\rho kT = 1 + \rho \sum_{ij} x_i x_j B_{ij} + \rho \sum_{ij} x_i x_j \alpha_{ij} [g_{ij}(d_i, d_j) - 1] \quad (1)$$

where P is the pressure, ρ is the number density, k is Boltzmann's constant, x_i and x_j are mole fractions, and the summations run over all components of the mixture. This equation contains three temperature-dependent parameters: B_{ij} (the second virial coefficient), α_{ij} (a scaling factor for the softness of the intermolecular repulsive forces), and b_{ij} (an analogue of the van der Waals covolume and related to α_{ij} by $b_{ij} = d(\alpha_{ij}T)/dT$). These parameters are related to the pair potential $U_{ij}(r)$ and are defined as follows:

$$B_{ij}(T) = 2\Pi \int_0^{\infty} (1 - e^{-U_{ij}/kT}) r^2 dr \tag{2}$$

$$\alpha_{ij}(T) = 2\Pi \int_0^{r_m} (1 - e^{-U_{ij}/kT}) r^2 dr \tag{3}$$

$$b_{ij}(T) = 2/3d_{ij}^3 = \alpha_{ij} + T d\alpha_{ij}/dT \tag{4}$$

where U_{ij}^0 is the repulsive part of U_{ij} and r_m is the position of the minimum in U_{ij} . Finally, $g_{ij}(d_i, d_j)$ in Eq. (1) is a pair distribution function at contact for mixtures of hard spheres and is defined in Ref. 13.

The reduced bulk modulus (reciprocal of the isothermal compressibility) can be calculated from Eq. (1), that is,

$$\begin{aligned} \underline{\mathbf{B}} = 1/kT(\partial P/\partial \rho)_T = & 1 + 2\rho \sum_{ij} x_i x_j \{ \alpha_{ij} [g_{ij}(d_i, d_j) - 1] + B_{ij} \} \\ & + \rho^2 \left[\sum_{ij} x_i x_j \alpha_{ij} dg_{ij}(d_i, d_j)/d\rho \right] \end{aligned} \tag{5}$$

or

$$\begin{aligned} 1 - \underline{\mathbf{B}} = & 2\rho \sum_{ij} x_i x_j \{ \alpha_{ij} [1 - g_{ij}(d_i, d_j)] - B_{ij} \} \\ & - \rho^2 \left[\sum_{ij} x_i x_j \alpha_{ij} dg_{ij}(d_i, d_j)/d\rho \right] \end{aligned} \tag{6}$$

We have chosen binary liquid mixtures of LJ molecules at three temperatures, in which one component has a fixed parameter value ($\epsilon_1/k = 34$ K and $\sigma_1 = 2.85$ Å), while the parameter values of the other component are $\epsilon_2/\epsilon_1 = 3.5$ and $\sigma_2/\sigma_1 = 2$. The unlike parameters ϵ_{12} and σ_{12} are taken to follow simple combining rules: $\sigma_{12} = \frac{1}{2}(\sigma_1 + \sigma_2)$ and $\epsilon_{12} = (\epsilon_1 \epsilon_2)^{1/2}$. Figures 1 to 4 show the isotherms of $1 - \underline{\mathbf{B}}$ vs x_1 for different densities in terms of the Boyle density, namely, $\rho_{12}B$.

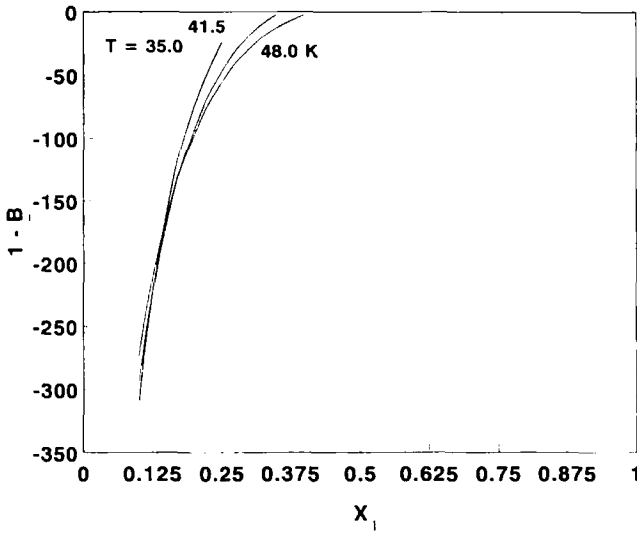


Fig. 1. Isotherms of $1-B$ vs X_1 at different temperatures for the liquid Lennard-Jones (12,6) mixtures (density is $0.9\rho_{12}B$).

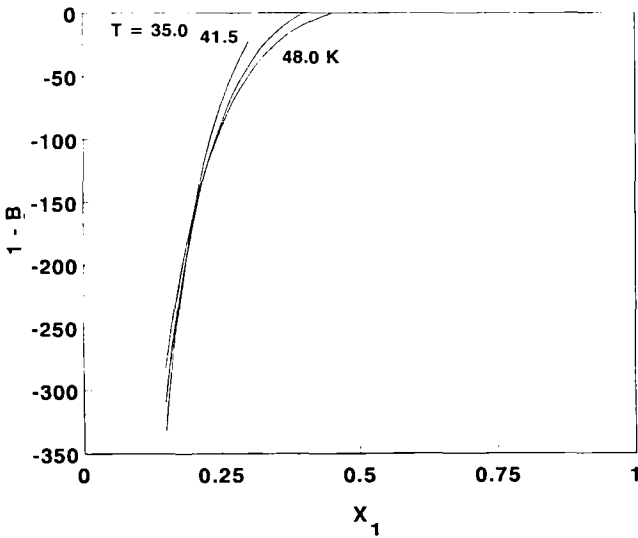


Fig. 2. Same as Fig. 1; the density is $\rho_{12}B$.

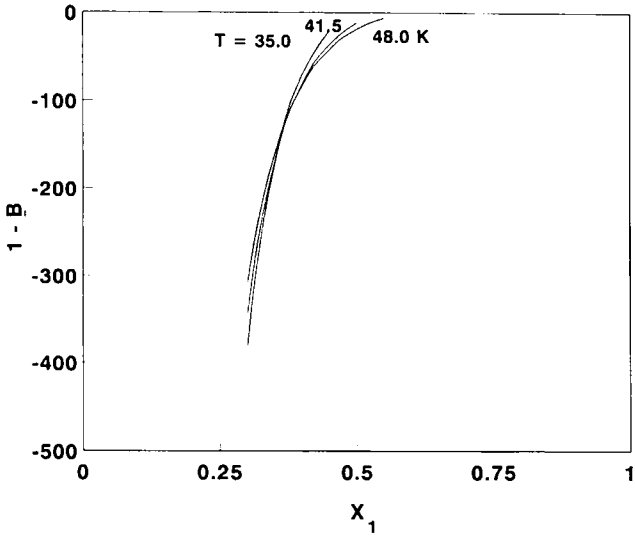


Fig. 3. Same as Fig. 1; the density is $1.2\rho_{12}B$.

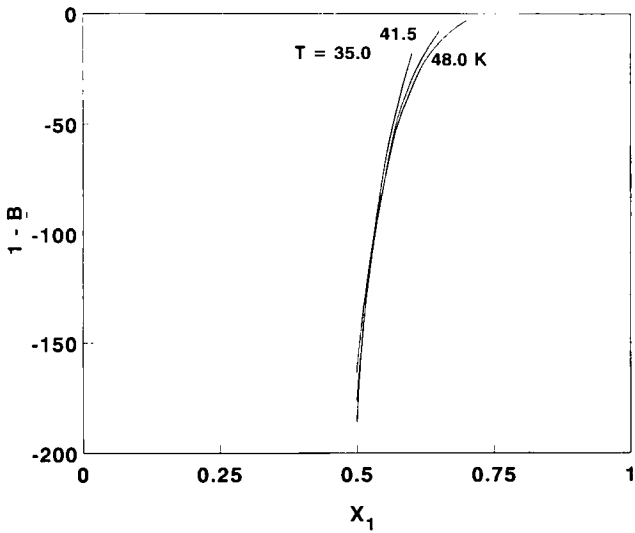


Fig. 4. Same as Fig. 1; the density is $1.5\rho_{12}B$.

The equation of state used for real fluid mixtures has the form

$$P/\rho kT = 1 + \rho \sum_{ij} x_i x_j (B_{ij} - \alpha_{ij}) F_{ij} + \rho \sum_{ij} x_i x_j \alpha_{ij} G_{ij} \quad (7)$$

where F_{ij} and G_{ij} have been defined in Ref. 14, and where the other parameters are the same as those in Eq. (1). From this equation, it follows that the reduced bulk modulus for real fluid mixtures has the form

$$1 - \underline{B} = 2\rho \sum_{ij} x_i x_j \{ \alpha_{ij} (F_{ij} - G_{ij}) - B_{ij} F_{ij} \} - \rho^2 \sum_{ij} x_i x_j \{ (B_{ij} - \alpha_{ij}) dF_{ij}/d\rho + \alpha_{ij} dG_{ij}/d\rho \} \quad (8)$$

We have tested this equation on the systems Ar + Kr, Kr + Xe, and $\text{CO}_2 + \text{C}_2\text{H}_6$. We have used the best available intermolecular potentials of the HFD-B or HFD-C forms as given by Aziz and co-workers [15–18] for Ar–Ar, Kr–Kr, Xe–Xe, Ar–Kr, and Kr–Xe. Figures 5 to 8 show the isotherms of $1 - \underline{B}$ vs x_{Ar} for Ar–Kr. This intersection occurs at the range of 1.4 up to $1.7\rho_{12}B$. The intersection range for Kr + Xe is the same as Ar + Kr. Typical isotherms are shown for Kr + Xe in Fig. 9.

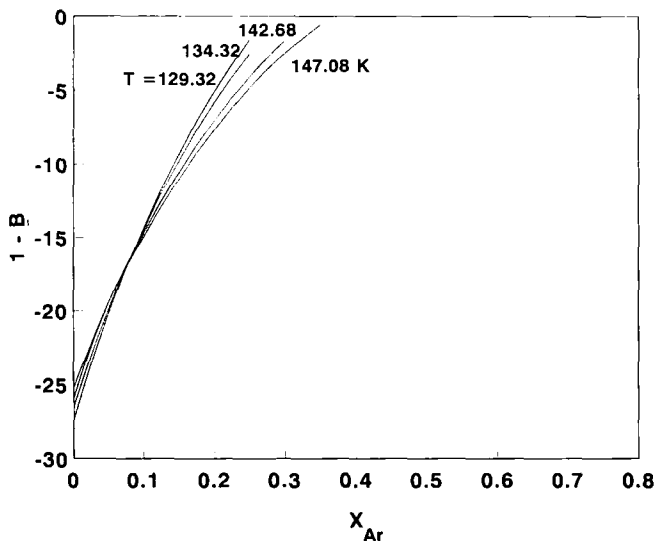


Fig. 5. Isotherms of $1 - \underline{B}$ vs x_{Ar} for Ar + Kr liquid mixtures at four temperatures. The density is $1.4\rho_{12}B$.

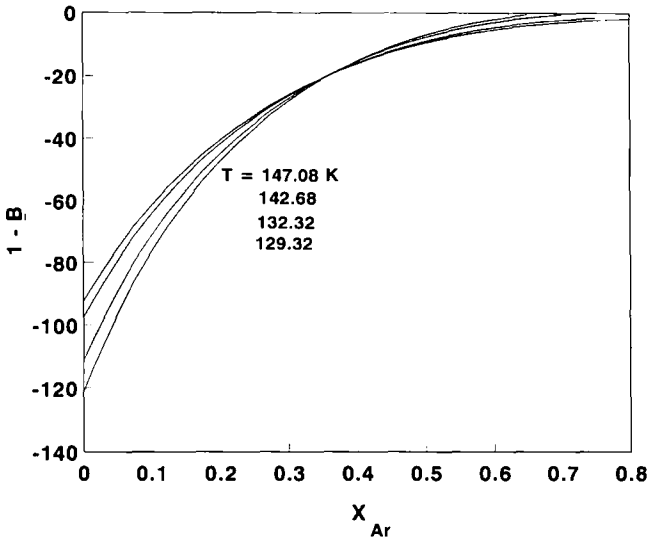


Fig. 6. Same as Fig. 5; the density is $1.5\rho_{12}B$.

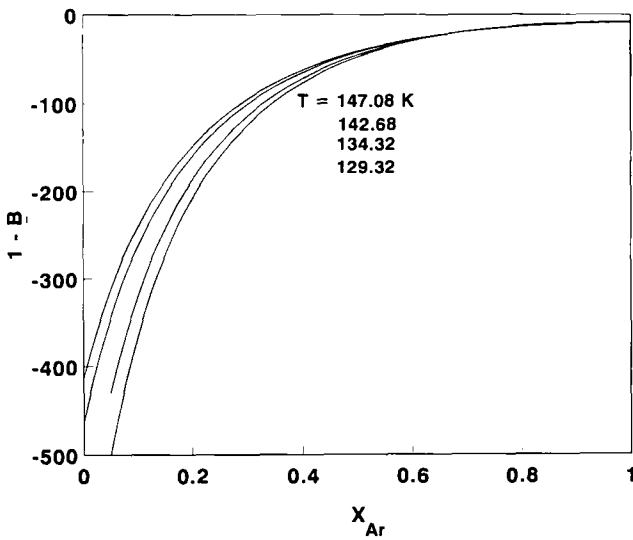


Fig. 7. Same as Fig. 5; the density is $1.6\rho_{12}B$.

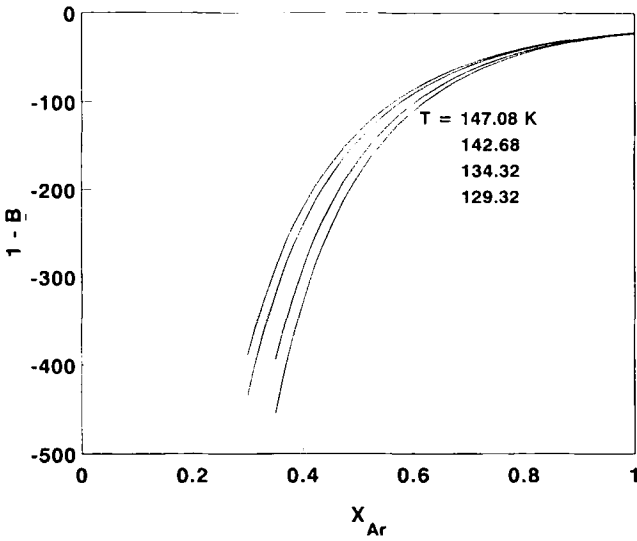


Fig. 8. Same as Fig. 5; the density is $1.7\rho_{12}B$.

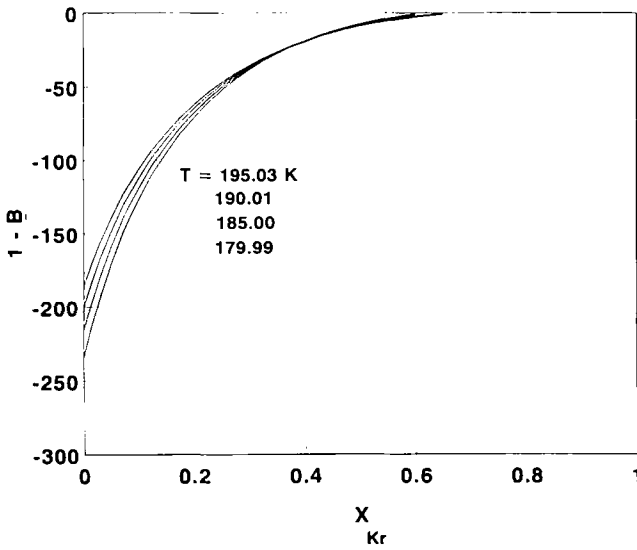


Fig. 9. Typical isotherms of $1-B$ vs X_{Kr} for Kr+Xe liquid mixtures at density $= 1.5\rho_{12}B$.

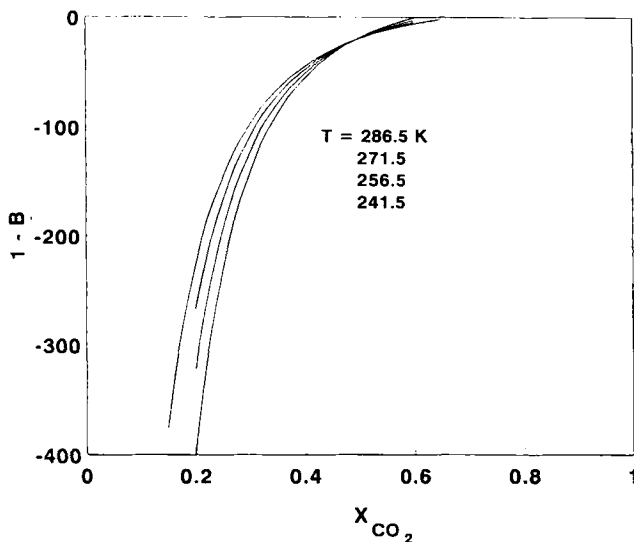


Fig. 10. Typical isotherms of $1 - B$ vs X_{CO_2} for $\text{CO}_2 + \text{C}_2\text{H}_6$ liquid mixtures at density $= 1.7\rho_{12}B$.

The values of $\alpha(T)$ and $b(T)$ for pure CO_2 and C_2H_6 can be calculated from Table I in Ref. 19. It is, however, important to use accurate experimental values of $B(T)$ in the calculations. The major information missing for this system concerns the CO_2 - C_2H_6 interaction. Therefore, we must use combination rules to find the parameters of a mean effective (12,6) potential for the CO_2 - C_2H_6 interaction and use this potential to calculate $B_{12}(T)$, $\alpha_{12}(T)$, and $b_{12}(T)$. We have adopted the fairly elaborate combination rules developed by Bzowski et al. [20] for use in a correlation scheme for the properties of low-density gas mixtures [21]. The intersection region for CO_2 - C_2H_6 is in the range of $1.4\rho_{12}B$ - $1.9\rho_{12}B$. A typical result for $\text{CO}_2 + \text{C}_2\text{H}_6$ is shown in Fig. 10.

3. CONCLUDING REMARKS

A new regularity, namely, a common intersection point for the isotherms of the reduced bulk modulus as a function of composition, has been found. This regularity has been applied for compressed liquid mixtures. The regularity holds for each liquid mixture over a specific range of densities.

From a careful examination of Figs. 1-10, it appears that the work reported here contains three points of particular interest.

- (i) The isotherms do not intersect at exactly the same composition, but they are within 5% of a common point.
- (ii) The lower-temperature isotherms tend to intersect at the smaller composition and the higher-temperature isotherms at the larger composition.
- (iii) The common modulus point is located at larger values of composition as the density increases for a particular mixture.

The most important conclusion of the present work is that the presence of a common intersection point has a strong basis in statistical mechanics. This regularity provides a significant constraint on equations of state for liquid mixtures.

REFERENCES

1. J. A. Beattie and W. H. Stockayer, *Rep. Prog. Phys.* **7**:1950 (1940).
2. R. L. Scott, *J. Chem. Educ.* **30**:542 (1953).
3. J. S. Rowlinson and F. L. Swinton, *Liquids and Liquid Mixtures* (Butterworth, London, 1982).
4. A. T. J. Hayward, *Br. J. Appl. Phys.* **18**:965 (1967).
5. J. R. Macdonald, *Rev. Mod. Phys.* **41**:316 (1969).
6. J. H. Dymond and R. Malhotra, *Int. J. Thermophys.* **9**:941 (1988).
7. D. Ber-Amotz and D. R. Herschbach, *Isr. J. Chem.* **30**:59 (1990).
8. J. Xu and D. R. Herschbach, *J. Phys. Chem.* **96**:2307 (1992).
9. Y. H. Hung and J. P. O'Connell, *Fluid Phase Equil.* **37**:75 (1987).
10. A. Boushehri, F. M. Tao, and E. A. Mason, *J. Phys. Chem.* **97**:2711 (1993).
11. A. Boushehri and E. K. Goharshadi, *Thermochim. Acta* **269**:371 (1995).
12. G. Parsafar and E. A. Mason, *J. Phys. Chem.* **97**:9048 (1993).
13. G. Ihm and E. A. Mason, *Mol. Phys.* **71**:109 (1990).
14. G. Ihm, Y. Song, and E. A. Mason, *Mol. Phys.* **75**:897 (1992).
15. R. A. Aziz and M. J. Slaman, *Mol. Phys.* **58**:697 (1986).
16. R. A. Aziz and M. J. Slaman, *Mol. Phys.* **57**:825 (1986).
17. R. A. Aziz, J. Presley, U. Buck, and J. Schleusener, *J. Chem. Phys.* **70**:4737 (1979).
18. R. A. Aziz and A. Dalen, *J. Chem. Phys.* **78**:2402 (1983).
19. Y. Song and E. A. Mason, *J. Chem. Phys.* **91**:7840 (1989).
20. J. Bzowski, E. A. Mason, and J. Kestin, *Int. J. Thermophys.* **9**:131 (1989).
21. J. Bzowski, J. Kestin, E. A. Mason, and F. J. Uribe, *J. Phys. Chem. Ref. Data* **19**:1179 (1990).