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# Thermodynamic regularities in compressed liquids:

## II. The reduced bulk modulus

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### Abstract

In a previous work, we analysed some regularities found in the behaviour of the thermal expansion coefficient,  $\alpha_p$ , in compressed liquids. We confirmed that a given liquid presents a characteristic pressure range in which the condition  $(\partial\alpha_p/\partial T)_p = 0$  is fulfilled within a narrow range of reduced densities. We also found that the density at which the condition  $(\partial\alpha_p/\partial T)_p = 0$  is satisfied,  $\rho_\alpha$ , decreases with temperature, a key feature not described before. Earlier studies by other authors suggested that similar regularities are expected for the reduced bulk modulus,  $B$ . We present here a detailed analysis of the temperature and density dependence of  $B$  from existing experimental results at high pressures. Several liquids have been analysed: argon, krypton, xenon, ethylene, tetrafluoromethane, trifluoromethane, carbon dioxide, carbon disulfide, *n*-butane, *n*-hexane, toluene, ethanol, 1-hexanol, *m*-cresol, and quinoline. We locate that the density  $\rho_B$  that fulfils the condition  $(\partial B/\partial T)_\rho = 0$  occurs at a particular region of the phase diagram, between 3.4 and 2.4 times the critical density of each liquid. Interestingly, the previously found density  $\rho_\alpha$  is close to  $\rho_B$ , in a similar region of the reduced phase diagram. However, we note that  $\rho_B$  typically decreases to a lesser extent with temperature than  $\rho_\alpha$ . In addition, we have found that  $\rho_B(T)$  behaves in a parallel fashion for the different liquids, showing larger values of  $\rho_B$  as the complexity of the molecules increases. These findings provide a strong basis for developing general equation of state models to describe the behaviour of liquids in the high-pressure regime.

### 1. Introduction

The development of simple models to describe the thermodynamic behaviour of liquids is a difficult task, due to the diversity of molecular interactions that the liquid state presents. In this

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regard, the study of the volumetric behaviour and the equation of state (EOS) of liquids provides an indirect way to understand the role played by the intermolecular forces. Two properties of special interest are the isothermal compressibility,  $\kappa_T$ ,

$$\kappa_T = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T = \frac{1}{\rho} \left( \frac{\partial \rho}{\partial p} \right)_T, \quad (1)$$

and the thermal expansion coefficient,  $\alpha_p$ ,

$$\alpha_p = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p = -\frac{1}{\rho} \left( \frac{\partial \rho}{\partial T} \right)_p. \quad (2)$$

The analysis of the behaviour of these two thermo-mechanical coefficients provides a more realistic picture of the interactions present in the liquid state, because both quantities are quite sensitive to subtle changes in the density. In addition, both can be accurately measured over wide ranges of pressure and temperature with several experimental techniques [1].

The pressure dependence of  $\alpha_p$  has been extensively studied from the experimental point of view for a number of liquids. A general observation is that  $\alpha_p(p)$  always decreases with pressure at constant temperature. There also exists a general agreement in that the  $\alpha_p(p)$  isotherms intersect at high pressures for many liquids, a characteristic feature first described by Bridgman [2], then by Cutler *et al* [3], and Jenner and Millet [4]. Randzio and Deiters concluded that the existence of such characteristic crossings is a key feature for examining available EOS models [5]. In a preceding paper, we have analysed  $\alpha_p(p, T)$  data for a number of different liquids [6]. The liquids studied were selected according to two criteria: availability of the experimental data over wide ranges of pressure and temperature (from the melting point up to the critical point), and liquids composed of molecules with different geometries and interactions. We confirmed that compressed liquids exhibit a general regularity: a given liquid presents a characteristic pressure range in which the condition  $(\partial \alpha_p / \partial T)_p = 0$  is fulfilled, i.e., an increase of the pressure modifies the curvature of the density isobars. For all the liquids considered, the crossing pressures fall between 0 and 400 MPa, typically below 200 MPa [6]. Furthermore, the condition  $(\partial \alpha_p / \partial T)_p = 0$  was found to occur within a relatively narrow range of reduced densities (between 3.5 and 2.2 times the critical density,  $\rho_c$ ). The density at which the previous condition is satisfied,  $\rho_\alpha$ , decreases with temperature. In general, at reduced temperatures of about 0.4 it is about three times  $\rho_c$ , while in the vicinity of the critical point it reaches a value around 2.5 times  $\rho_c$ . To the best of our knowledge, this feature was described for the first time in [6].

Thermodynamic regularities associated to the behaviour of  $\kappa_T$  have been instead described through the analysis of the so-called reduced bulk modulus,  $B$ , which is defined as

$$B \equiv \left( \frac{\partial}{\partial \rho} \left( \frac{p}{RT} \right) \right)_T = \frac{1}{RT} \left( \frac{\partial p}{\partial \rho} \right)_T = \frac{1}{RT \rho \kappa_T}, \quad (3)$$

where  $R$  is the gas constant. Note that the definition of this quantity differs from that of the bulk modulus, the inverse of  $\kappa_T$ , which is a key property for studying the EOS of solids.

Huang and O'Connell [7] examined the behaviour of  $B$  for more than 250 substances, and they concluded that for each substance there exists a density where  $B$  seems to be independent of temperature, i.e., the isotherms of  $B(\rho)$  also present a characteristic crossing point (a brief discussion of their study is included in section 2). Hence, it seems that density is the dominant variable in determining the behaviour of  $B$  and that temperature effects could be ignored. This feature indicates that  $B$  is the relevant quantity to search for regularities in dense liquids. Later, Boushehri *et al* performed a theoretical analysis of this finding using a statistical-mechanical-based EOS [8]. They pointed out that the isotherms of  $B$  do not intersect at exactly one point, but rather over a small range of density, and that such behaviour is restricted to temperatures

ranging between the triple and the critical points. As we shall confirm below, the temperature range examined by Huang and O'Connell was too narrow to observe such variation.

The subject of the present study concerns a detailed analysis of the behaviour of  $B$  for a variety of compressed liquids. Most liquids included in our analysis of  $\alpha_p$  [6] have been considered here as well. It is worth noting that, to carry out such analysis, available experimental data must cover wide ranges of temperature and pressure, since we are interested in knowing whether the intersections of  $B$  occur at a single point or whether they shift with temperature. In general, we have considered only those liquids with accurate experimental data available at high pressures from the melting temperature up to the critical temperature,  $T_c$ . Our ultimate goal is to compare and to relate the regularities in  $B$  with those found in  $\alpha_p$ . Such information provides an important support for developing general EOS models to describe the complex behaviour of liquids in the high-pressure/density regime.

## 2. Analysis of the reduced bulk modulus according to Huang and O'Connell

The reduced bulk modulus, as defined in equation (3), is a mechanical property that can be related to volume derivatives of the energy and entropy:

$$B = -V^2 \left[ \left( \frac{\partial^2(S/R)}{\partial V^2} \right)_T - \left( \frac{\partial^2(U/RT)}{\partial V^2} \right)_T \right]. \quad (4)$$

This quantity is of special theoretical interest because it can also be related to the spatial integral of the direct correlation function,  $c(r; \rho, T)$ , i.e.:

$$B = 1 - \rho \int c(r; \rho, T) \, dr. \quad (5)$$

By using data of  $n$ -nonane, Huang and O'Connell observed that the contribution of the energy term in equation (4) is the most important at high densities. They also pointed out that the isotherms for both the energy term and  $B$  cross [7]. The phenomenon of the intersections of  $B$  is observed in the dense liquid regime, where the fluid structure is considered similar to that of a hard fluid, and so the density dependence is the dominant term, as is the case for hard spheres. This reasoning led Huang and O'Connell to consider whether the behaviour of  $B$  can be reproduced by a hard fluid model. Comparison of experimental data to the expected hard body behaviour allows examining whether the intersections can be attributed to variations of repulsive forces and excluded volume effects or not. Huang and O'Connell, using experimental data for argon and  $n$ -nonane [7] found very different density dependence between the experimental data and the hard spheres model, so these authors concluded that attractive forces notably influence the density dependence of  $B$ .

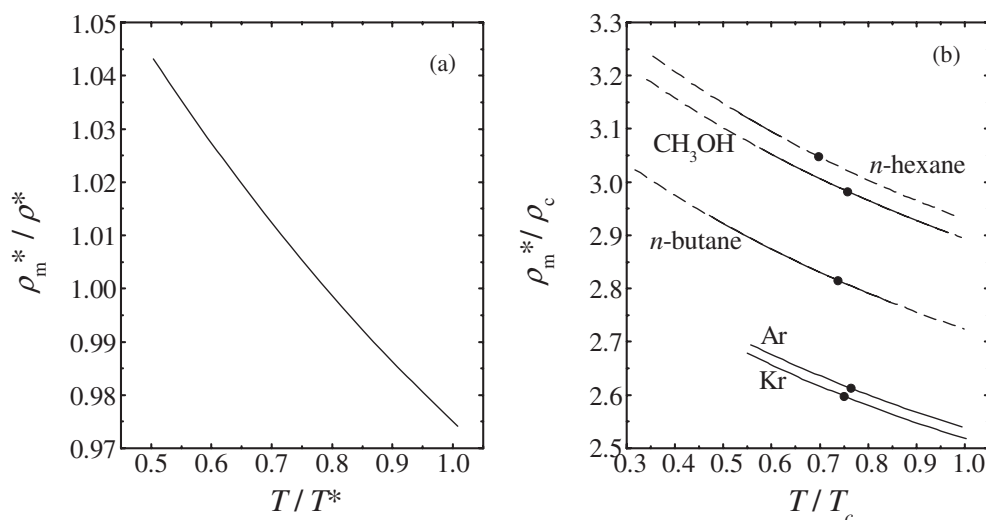
From the assumption that a single crossing point for  $B(\rho)$  exists, Huang and O'Connell [7] proposed the following corresponding states scheme for  $B$ :

$$B = B(\rho, T) = 1 - (1 - B^*) \sum_{i=0}^3 \sum_{j=0}^2 a_{ij} (\tilde{\rho})^i (\tilde{\tau})^j, \quad (6)$$

where  $\tilde{\rho} = (\rho/\rho^*)$  and  $\tilde{\tau} = (T^*/T)$ . To represent the EOS of a liquid within this correlation scheme, equation (3) must be integrated, i.e.:

$$p(T, \rho) = p(T, \rho_{\text{ref}}) + RT \int_{\rho_{\text{ref}}}^{\rho} \left[ 1 - (1 - B^*) \sum_{i=0}^3 \sum_{j=0}^2 a_{ij} (\tilde{\rho})^i (\tilde{\tau})^j \right] d\rho. \quad (7)$$

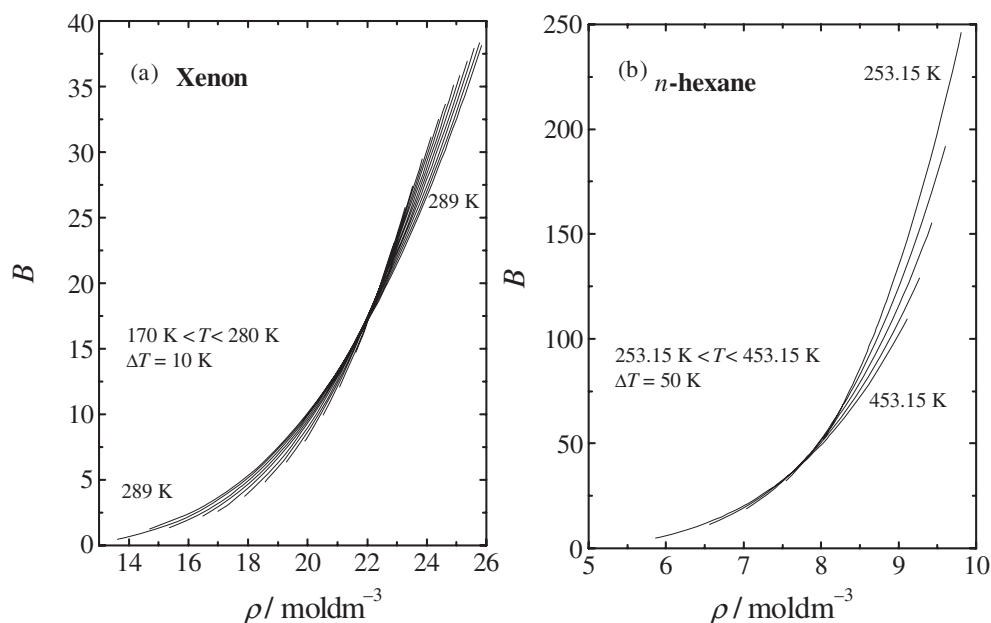
So, the complete EOS of a liquid is characterized by the parameters  $B^*$ ,  $\rho^*$  and  $T^*$ , with the knowledge of the isochoric thermal pressure coefficient,  $\gamma_V = (\partial p/\partial T)_V$ , along a reference isochore.



**Figure 1.** Temperature dependence of the density  $\rho_m^*$  where  $(\partial B / \partial T)_\rho = 0$  is satisfied by the equation (6), as derived from Huang and O'Connell [7]. (a) General behaviour as predicted by equation (6) in reduced parameters. (b) Real behaviour observed for selected liquids: argon, krypton, *n*-butane, *n*-hexane and methanol, in reduced units by the critical constants of each substance. Solid lines indicate the range used by Huang and O'Connell to obtain the characteristic parameters of each liquid. Dashed lines are the extrapolations over the whole liquid range. Full circles are the values of  $\rho_m^*$  given in [7].

Huang and O'Connell obtained the universal coefficients  $a_{ij}$  from available data of  $B$  for methane and *n*-nonane. They subsequently calculated the three characteristic parameters,  $B^*$ ,  $\rho^*$  and  $T^*$ , for a variety of liquids, assuming that these parameters contained the physical meaning of the crossing coordinates of  $B$ . In general, they obtained that  $T^*$  was close to the critical temperature, while  $\rho^*$  was about two or three times the critical density [7], revealing that the intersections of the  $B$  isotherms occur in the compressed regime of the liquid.

From the analysis of the high-pressure properties of several liquids, we noted that the assumption of a single crossing point for  $B(\rho)$  within the correlation scheme proposed by Huang and O'Connell, in fact, is not a general feature for most liquids. The reason for these discrepancies can be found if one examines equation (6) in detail. Thus, if one applies the condition  $(\partial B / \partial T)_\rho = 0$  to equation (6), one finds that the density where the condition is fulfilled (hereafter referred to as  $\rho_m^*$ ) shows a non-negligible decrease with increasing temperature. As schematically shown in figure 1(a), a decrease in  $\rho_m^*$  of about 7% is expected between reduced temperatures ranging from  $0.5T^*$  to  $T^*$ . We have calculated such variation for selected liquids studied by Huang and O'Connell in figure 1(b). We used the values of  $\rho_m^*$  (plotted as solid circles in the figure) and  $T^*$  reported by these authors. Our results clearly indicate that the crossing point for the isotherms of  $B$  of a given substance is not unique, so the characteristic parameters  $B^*$ ,  $\rho^*$  and  $T^*$  lose their original physical meaning. In particular,  $\rho^*$  corresponds approximately to a mean density in the range of densities where  $B$  is independent of the temperature along an isochore. As an example, let us briefly analyse the values obtained for liquid methanol, one of the liquids studied by Huang and O'Connell [7]. For this substance, within its liquid range ( $0.34T_c - T_c$ ),  $\rho_m^*$  varies from about 3.2 to 2.9 times  $\rho_c$ , and the value obtained for  $\rho_m^*$  was  $2.981\rho_c$  [7].

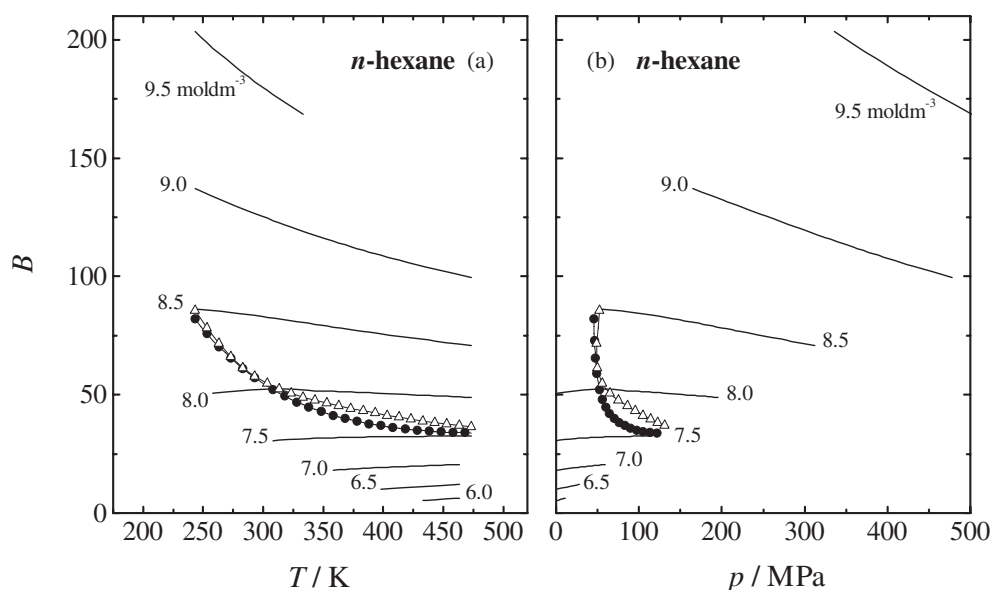


**Figure 2.** Reduced bulk modulus as a function of density at different temperatures for (a) xenon [18], and (b) *n*-hexane [9].

### 3. General analysis of the reduced bulk modulus

The previous analysis reveals certain analogies between the behaviour of  $B$  and that found for  $\alpha_p$  [6]. For this reason, we shall examine in detail the available experimental data of  $B$ . Some of the liquids studied here were already analysed by Huang and O'Connell [7], although in most cases we have extended the temperature range using additional experimental results. In figure 2 we plot several isotherms of  $B$  as a function of the density for xenon and *n*-hexane. Both liquids have been selected for our discussion because a detailed analysis of  $\alpha_p$  is available [6]. At constant temperature,  $B$  increases with increasing density for both liquids. It is also confirmed that the intersections of the  $B$  isotherms lie within a small density range (for xenon around 22 mol dm<sup>-3</sup>, and for *n*-hexane around 8 mol dm<sup>-3</sup>). As a consequence, at low densities  $B$  increases with both temperature and pressure and, at higher densities,  $B$  decreases with increasing temperature or pressure. Figure 3 illustrates this observation for *n*-hexane. The results of  $B$  have been obtained using data reported by Pruzan [9]. We also compare the coordinates  $(B, T)$  and  $(B, p)$  for the condition  $(\partial B / \partial T)_\rho = 0$  with those obtained using data from Randzio *et al* [10]. It is noticeable that both sets of data yield comparable results, in contrast with our previous observations for  $\alpha_p$ , where a slightly different trend for the condition  $(\partial \alpha_p / \partial T)_p = 0$  was observed between both datasets [6]. Let us say in passing that  $B$  has been calculated from  $\alpha_p$  measurements, so it is concluded that calculation of  $B$  (or  $\kappa_T$ ) does not depend to a great extent on the expressions used to represent  $\alpha_p$ , which is the main difference between the studies of Pruzan and Randzio *et al*.

Returning to the results of *n*-hexane plotted in figure 3, it is clearly observed that the density at which the condition  $(\partial B / \partial T)_\rho = 0$  is fulfilled (hereafter referred to as  $\rho_B$ ) decreases with increasing temperature for *n*-hexane. The isochores of  $B$  between 243 and 473 K display maxima within a small range of densities (between 8.45 and 7.55 mol dm<sup>-3</sup>),  $\rho_B$  varies between



**Figure 3.** Reduced bulk modulus of liquid *n*-hexane plotted against (a) temperature and (b) pressure. Numbers indicate the following isochores: 9.5, 9.0, 8.5, 8.0, 7.5, 7.0, 6.5 and 6.0 mol dm<sup>-3</sup>. Curves are derived from results of Pruzan [9]. Symbols represent the conditions where  $(\partial B/\partial T)_\rho = 0$ : open triangles have been calculated using data from Randzio *et al* [10], while full circles represent those obtained from the results of Pruzan [9].

3.11 and 2.78 times  $\rho_c$ , and the maxima are located at pressures between 45 and 122 MPa. Using the correlation scheme of Huang and O'Connell [7] described earlier,  $\rho_B$  decreases from 3.16 to 2.96 times  $\rho_c$  in the same range of temperatures (about a 10% decrease).

A similar analysis has been performed with the experimental data of  $B$  for a number of liquids. The results are summarized in table 1. We list the  $p\rho T$  region that meets the condition  $(\partial B/\partial T)_\rho = 0$ , summarized in figure 4. As we already observed for  $\alpha_p$  [6], the pressure range where the extrema of  $B$  are found rarely exceeds 150–200 MPa. However, the behaviour of  $B$  appears to be more regular than that of  $\alpha_p$ , in the sense that the  $B$  isochores exhibit a maximum for most of the liquids considered. In general, we find that the pressure at the maximum increases with increasing temperature. In contrast, we found that the isobars of  $\alpha_p(T)$  exhibit maxima, minima or both types of extrema [6]. In figure 4(b) we also note that  $\rho_B$  decreases with increasing temperature for most liquids, with the exception of trifluoromethane. In the case of liquid krypton and liquid xenon, an increase of  $\rho_B$  with increasing temperature is observed at temperatures close to the melting temperature. We argue that the limited number of experimental data available (due to solidification) does not allow for a good characterization of this region of the  $p\rho T$  surface and the derived properties of these liquids.

Interestingly, as occurred with the condition  $(\partial\alpha_p/\partial T)_p = 0$  [6], the condition  $(\partial B/\partial T)_\rho = 0$  takes place in a narrow range of densities (2.4–3.4 times the critical density) for all the liquids studied. At reduced temperatures of about 0.4,  $\rho_B$  (in reduced units) falls between 3.3 and 3.0, and near to the critical point  $\rho_B$  lies between 2.9 and 2.5. The decrease of  $\rho_B$  with increasing temperature is relatively small for all the liquids. As is confirmed in table 1, the largest variation found is about 16% for *n*-butane.

We have compared the results obtained for both conditions  $(\partial\alpha_p/\partial T)_p = 0$  and  $(\partial B/\partial T)_\rho = 0$ . For the sake of clarity, we have considered only four liquids (krypton,

**Table 1.** Liquids studied in this work presenting intersections in their  $B(\rho)$  isotherms.  $T_{\text{tp}}$  (K) is the triple point temperature,  $T_c$  (K) is the critical temperature,  $\Delta T$  (K) indicates the range of temperatures where experimental data are available,  $p_{\text{max}}$  (MPa) is the maximum pressure reached in the experiments. In the  $p\rho T$  region where the condition  $(\partial B/\partial T)_\rho = 0$  is fulfilled:  $\Delta p_B$ , pressure range in MPa;  $\Delta T_B$ , temperature range in K;  $\Delta T_{B,\text{red}}$ , reduced temperature range; and  $\Delta \rho_{B,\text{red}}$ , reduced density range. Reduced quantities,  $T_{B,\text{red}} = T_B/T_c$  and  $\rho_{B,\text{red}} = \rho_B/\rho_c$ , with  $T_c$  and  $\rho_c$  the critical temperature and density, respectively. Data sources are listed in the last column.

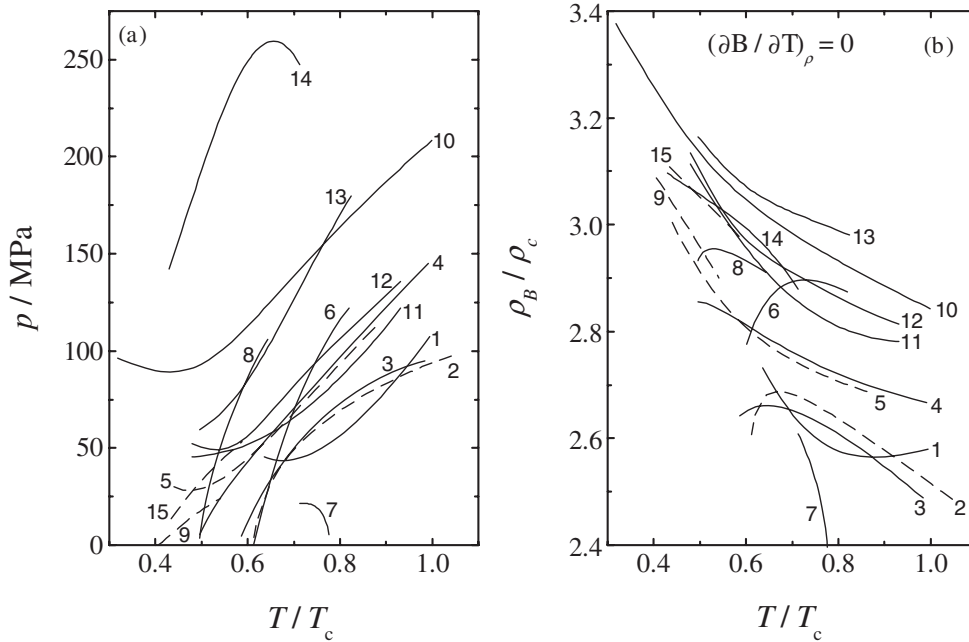
Liquid	$T_{\text{tp}}$	$T_c$	$\Delta T$	$p_{\text{max}}$	$\Delta p_B$	$\Delta T_B$	$\Delta T_{B,\text{red}}$	$\Delta \rho_{B,\text{red}}$	References
Argon	83.8	150.8	86–150	320	45–107	96–150	0.64–0.99	2.73–2.56	[16]
Krypton	115.8	209.4	120–220	373	0–98	128–220	0.61–1.05	2.69–2.48	[17]
Xenon	161.3	289.74	165–289	385	5–95	170–289	0.59–1.00	2.66–2.49	[18]
Ethylene	103.97	282.35	110–280	130	5–145	140–280	0.50–0.99	2.86–2.67	[19]
CF <sub>4</sub>	86.4	227.45	95–413	110	30–113	100–200	0.44–0.88	3.00–2.68	[20, 21]
CHF <sub>3</sub>	110.0	299.1	126–332	100	5–104	185–230	0.62–0.77	2.82–2.89	[21]
CO <sub>2</sub>	216.56	304.21	220–304	400	5–22	220–236	0.72–0.78	2.59–2.40	[22]
CS <sub>2</sub>	161.3	549.4	246–353	400	3–106	272–353	0.50–0.64	2.95–2.91	[23]
<i>n</i> -butane	134.8	425.16	135–425	400	90–209	135–425	0.32–1.00	3.38–2.84	[22]
<i>n</i> -hexane	177.8	507.8	238–472	762	45–122	243–473	0.48–0.93	3.11–2.78	[9]
Toluene	178.0	591.77	200–480	400	0–78	280–320	0.47–0.54	3.07–3.04	[24]
Ethanol	158.37	513.9	193–333	280	14–54	223–303	0.43–0.59	3.11–2.97	[25]
1-hexanol	229.2	610.7	303–503	400	60–180	303–503	0.50–0.82	3.16–2.98	[26]
<i>m</i> -cresol	285.4	705.8	303–503	400	142–259	303–503	0.43–0.71	3.10–2.88	[27]
Quinoline	258.0	782.0	303–503	400	86–109	303–503	0.39–0.64	8.76–7.76 <sup>a</sup>	[28]

<sup>a</sup> Density values in units of mol dm<sup>-3</sup>.

ethylene, *n*-butane and *n*-hexane) in the comparison as plotted in figure 5. The results have been reproduced from figure 4 of this work and figure 3 of [6]. It is noteworthy that the densities in which each condition take place,  $\rho_\alpha$  and  $\rho_B$ , respectively, lie in the same region of the reduced phase diagram, although  $\rho_\alpha$  shows a larger variation with the temperature than  $\rho_B$  (for instance, in krypton,  $\rho_\alpha$  decreases by about 12% whereas  $\rho_B$  decreases by about 7% within the same temperature range). Thus, it is observed that  $\rho_\alpha > \rho_B$  at low temperatures, but due to the smaller variation of  $\rho_B(T)$ ,  $\rho_\alpha < \rho_B$  at high temperatures. In general, the curves of  $\rho_\alpha(T)$  are closer for the different liquids, whereas those of  $\rho_B(T)$  seems to exhibit a certain parallel behaviour. In any case, the most interesting feature in figure 5 is that both conditions are fulfilled simultaneously in a similar region of the reduced phase diagram with slightly different temperature variations.

Hence, it can be inferred that a close relationship may exist between both regularities. To the best of our knowledge, a molecular interpretation of the crossings in the  $\alpha_p$  isotherms has only been attempted by Jenner and Millet [4], and Randzio [11]. Jenner and Millet in their study of alkyl bromides (from two up to nine carbon atoms) found a change in the curvature of the density isobars at high pressures. These authors attributed such change to the predominant influence of anharmonic effects on the intermolecular vibrations in the interaction energy. At low pressures, the anharmonic contribution is negligible, and the volume is proportional to  $T^{3/2}$ . At moderate pressures, the importance of the anharmonic terms increases, and the isobars are apparently rectilinear, while at very high pressures the volume scales to  $T^{3/n}$ , with  $n > 3$  [4]. With regards to Randzio's observations [11], he concluded that the intersections reflect a pressure-induced change in the shape of the effective intermolecular potential. Perhaps the most interesting consequence of this conclusion is that any EOS based on an invariant intermolecular potential function is unable to give a proper description of the  $\alpha_p$  behaviour of dense liquids.





**Figure 4.** (a) Pressures and (b) reduced densities ( $\rho_B/\rho_c$ ) where  $(\partial B/\partial T)_\rho = 0$  as functions of reduced temperature ( $T/T_c$ ) for several liquids. 1: argon [16], 2: krypton [17], 3: xenon [18], 4: ethylene [19], 5:  $\text{CF}_4$  [20], 6:  $\text{CHF}_3$  [21], 7: carbon dioxide [22], 8: carbon disulfide [23], 9: carbon disulfide [29], 10: *n*-butane [22], 11: *n*-hexane [9], 12: *n*-hexane [10], 13: 1-hexanol [26], 14: *m*-cresol [27] and 15: ethanol [25].

#### 4. Discussion

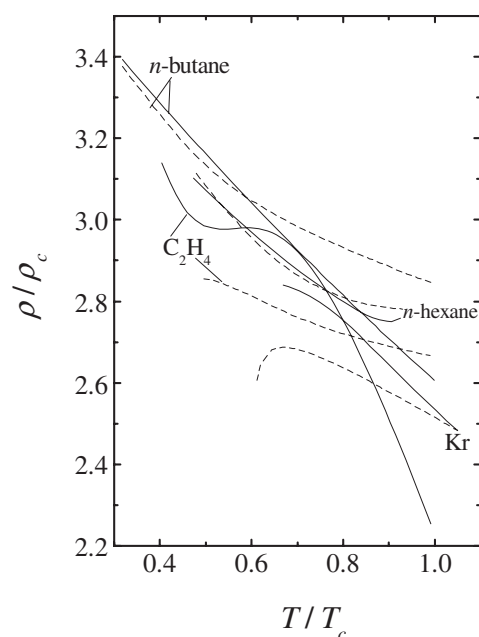
There have been several attempts to provide a theoretical basis for the observed behaviour in  $B$  [8, 12, 13]. Najafi *et al* [12] concluded that, at the density of a common  $B$ , the average intermolecular separations are such that the attraction and repulsion have equal contributions to  $B$ , but opposite in sign. In our opinion, a more interesting analysis is that of Boushehri *et al* [8]. These authors expected that a single crossing point for  $B$  could reveal some characteristic feature of the molecular fluid structure. Using a statistical–mechanical-based EOS [8], they concluded that the van der Waals EOS does not lead to intersections in the  $B$  isotherms because the covolume is independent of temperature. By using the improved Ihm–Song–Mason EOS [14], they concluded that if  $B$  intersects at a single density, its value at low temperatures could be approximated as

$$\rho_{B0} \approx 1/\lambda b(0), \quad (8)$$

where  $b(0)$  is the molecular covolume at zero temperature, which gives a measure of the molecular size in terms of the range of the repulsive forces,  $r_m$ :

$$b(0) = (2\pi/3)r_m^3. \quad (9)$$

The parameter  $\lambda$  in equation (8) is a characteristic constant of the substance, which equals 0.454 for noble-gas fluids, and decreases for more complex fluids, so it can be regarded as a molecular shape parameter. We have calculated  $\rho_{B0}$  for some liquids by using equation (8) and parameters given in [14], obtaining the following results:  $\rho_{B0}(\text{N}_2) = 2.41$ ,  $\rho_{B0}(\text{CO}_2) = 2.47$ ,  $\rho_{B0}(\text{SF}_6) = 2.55$ ,  $\rho_{B0}(\text{CF}_4) = 2.71$ ,  $\rho_{B0}(\text{CH}_4) = 2.24$ ,  $\rho_{B0}(\text{ethane}) = 2.46$ ,  $\rho_{B0}(\text{propane}) = 2.46$ , and  $\rho_{B0}(\textit{n}\text{-butane}) = 2.49$ , in reduced units by the critical density.



**Figure 5.** Reduced densities ( $\rho/\rho_c$ ) as a function of reduced temperature ( $T/T_c$ ) where the two conditions, (—)  $(\partial\alpha_p/\partial T)_p = 0$  and (- - -)  $(\partial B/\partial T)_p = 0$ , are fulfilled for selected liquids: krypton [17], ethylene [19], *n*-butane [22] and *n*-hexane [9].

These theoretical predictions are in good agreement with our results of figure 4(b). It is evident that the extrema in  $B$  deduced from experimental data exhibit a similar behaviour over the whole temperature range. Thus, the noble-gas fluids present the lowest values of  $\rho_B(T)$ , and an increase in the size of the constituent molecules leads to an increase in  $\rho_B(T)$ . This might explain the apparent parallel behaviour found for  $\rho_B(T)$  among the different liquids studied here.

Gregorowicz *et al* analysed different EOS models to evaluate the influence of the functional form in the shape of the  $B$  isochores [13]. They found that an inversion in  $B$  is not expected from polynomial forms, and that only a modified Benedict–Webb–Rubin model resembles such behaviour. In this regard, we emphasize the importance of the present study (which is based on direct analysis of experimental results of  $B$ ) in the development of thermodynamic models of general applicability, with reasonable capabilities in providing accurate derived properties in the compressed liquid regime. In fact, we have already used the regular behaviour of  $B$  described here to obtain universal functions to represent the temperature dependence of the characteristic parameters of the so-called spinodal EOS [15]. This will be the subject of a forthcoming paper.

## 5. Conclusion

The regular behaviour of the reduced bulk modulus,  $B$ , has been analysed using experimental data of several compressed liquids (argon, krypton, xenon, ethylene, tetrafluoromethane, trifluoromethane, carbon dioxide, carbon disulfide, *n*-butane, *n*-hexane, toluene, ethanol, 1-hexanol, *m*-cresol, quinoline). We have verified that the intersections of the  $B$  isotherms as a function of the density occur within a narrow density range. In general, the  $B$  isochores

exhibit maxima at pressures that rarely exceed 150–200 MPa, although these pressures tend to increase with increasing temperature. The density at which the condition  $(\partial B/\partial T)_\rho = 0$  is fulfilled,  $\rho_B$ , is found in a particular region of the phase diagram, i.e., between 3.4 and 2.4 times the critical density of the liquid. In addition, the curves of  $\rho_B(T)$  appear to exhibit a certain parallel behaviour for the different liquids. Finally, it appears that liquids formed by more complex molecules tend to exhibit larger values of  $\rho_B$ ; this is an observation in good agreement with theoretical predictions. Finally, it is worth noting that a similar regularity described in  $\alpha_p$ , characterized by  $\rho_\alpha$ , takes place in the same region of the reduced phase diagram, although  $\rho_\alpha$  exhibits more pronounced temperature dependence in all cases. The occurrence of both regularities in the same range of reduced densities provides a basis for developing EOS models of general applicability in compressed liquids.

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