Thermodynamic regularities in compressed liquids: I. The thermal expansion coefficient

Thermodynamic regularities in compressed liquids: I. The thermal expansion coefficient

Mercedes Taravillo, Valentín G Baonza[1]**, Mercedes Cáceres and Javier Núñez**

Departamento de Química Física I, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, 28040-Madrid, Spain

E-mail: vgbaonza@quim.ucm.es

Abstract
We analyse here the thermodynamic behaviour of the thermal expansion coefficient for a number of liquids. The purpose of this work is to provide some general rules to develop equations of state models meeting the following criteria: thermodynamic consistency, generality, predictive power and accuracy to represent derived properties over wide ranges of pressure and temperature. The liquids included into our analysis have been selected to meet two criteria: (1) available experimental data over wide ranges of pressure and temperature (from the melting point up to the critical point), and (2) liquids composed of molecules with different geometries and interactions.

1. Introduction

The thermodynamic behaviour of the liquid state is by far the most difficult to understand and to predict due to the inherent complexity of this state of matter, as a consequence of the diversity of molecular interactions involved. A general observation is that liquids composed of non-polar and polar molecules exhibit a quite distinct thermodynamic behaviour, especially in those regions of the phase diagram where different molecular interactions are comparable in energy. For instance, hydrogen bonding and molecular packing effects are often responsible for anomalies in the expected thermodynamic behaviour of liquids.

Density variations along isothermal or isobaric paths are usually smooth functions of pressure and temperature. However, properties such as the isothermal compressibility, κ_T, and the thermal expansion coefficient, α_p, are quite sensitive to subtle changes in the density. Although there exist several pressure–volume–temperature (p, V, T) databases in tabulated form, there is a general tendency to compile equation of state (EOS) results in algebraic form. More often than would be desirable, the pressure and temperature dependencies of the derived properties are imposed by the algebraic form of the EOS used to correlate the (p, V, T) data, resulting in a severe lost of information contained in the original results.

---

[1] Author to whom any correspondence should be addressed.

The most important defect commonly found in current EOS models of liquids is their lack of predictive power and their inability to represent with enough reliability the corresponding derived properties. These limitations are often a direct consequence of the algebraic form used to correlate experimental pressure–volume–temperature data. Therefore, any attempt to develop a model of EOS of general applicability in liquids requires the inclusion of general thermodynamic constraints. The obvious solution to this problem concerns the search for simple but accurate phenomenological expressions to describe the general trends observed for the derived properties, obtaining the desired EOS in (p, V, T) variables by integration [1]. This is not an easy task though, because the number of exceptions found in the thermodynamic behaviour of liquids exceeds the number of regularities. Consequently, many authors use polynomials or extensions of simple EOS to fit a given experiment. Cubic EOSs derived from the van der Waals equation are well-known examples for physicists, chemists and engineers [2].

The analysis of EOS models in terms of derived properties such as α_p or κ_T has interesting advantages, since both are related to the first derivatives of the (p, V, T) EOS, and both can be accurately measured over wide ranges of pressure and temperature by different experimental techniques [3]. Although a general discussion of the behaviour of these properties for different types of liquids is still lacking, the pressure behaviour of the α_p isotherms has been a matter of interest due to the characteristic crossings observed for this property at high pressure. In this regard, Randzio and Deiters [4] concluded that this is a key feature to examine EOS models.

To the best of our knowledge, a molecular interpretation of this observation has only been attempted by Jenner and Millet [5, 6], and Randzio [7]. Jenner and Millet [5, 6] in their studies on alkyl bromides found that $(\partial^2 V/\partial T^2)_p$ changes sign between 250 and 300 MPa. These authors observed a curvature change of the isobars at a given pressure, the change being attributed to the predominant influence of the anharmonicity of the intermolecular vibrations. Randzio [7] also concluded that the intersections reflect a change in the effective intermolecular potential with pressure due to anharmonic effects. Perhaps the most interesting consequence of this conclusion is that any EOS based on a constant form of an intermolecular potential will be unable to describe the thermodynamic behaviour of liquids. Thus, semiempirical approaches are required to correlate experimental data so far.

The purpose of this paper is therefore to analyse the thermodynamic behaviour of the thermal expansion coefficient for a number of liquids of different nature. The liquids included in our analysis have been selected to meet two criteria:

 (1) available experimental data over wide ranges of pressure and temperature (from the melting point up to the critical point), and
 (2) liquids composed of molecules with different geometries and interactions.

Our ultimate goal is to develop universal EOS models for liquids meeting the criteria of thermodynamic consistency, predictive power and accuracy to represent derived properties over wide ranges of pressure and temperature. We have not included liquid water in our discussion because it records a number of irregularities that make it a difficult task finding similarities with other liquids. However, the current approach raises some ideas to derive an appropriate model for this important liquid within the same framework.

2. Results and discussion

2.1. Regularities in α_p as a function of pressure and temperature

The pressure dependency of the thermal expansion coefficient of liquids has been extensively studied from the experimental point of view. A general observation is that $\alpha_p(p)$ always
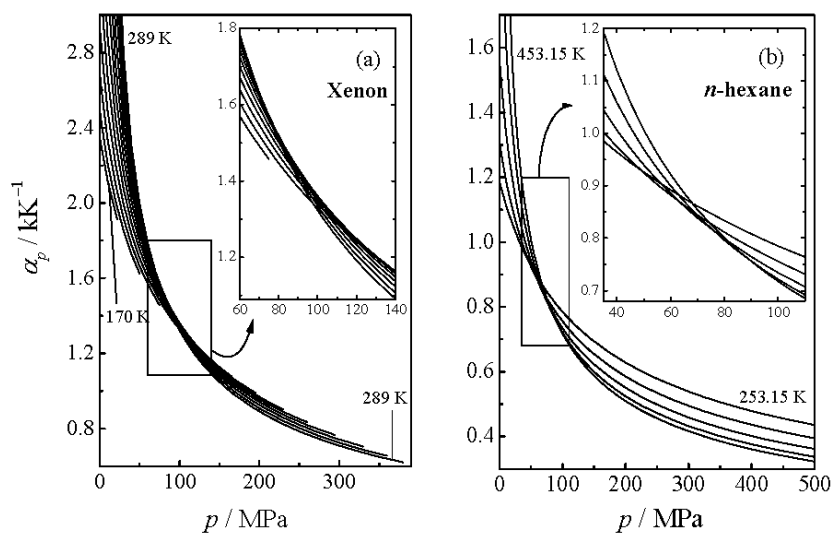
Figure 1. Thermal expansion coefficient as a function of pressure at different temperatures. (a) Xenon [27]: 170, 180, 190, 200, 210, 220, 230, 240, 250, 260, 270, 280 and 289 K, and (b) n-hexane [17]: 253.15, 303.15, 353.15, 403.15 and 453.15 K. The intersection regions have been expanded in both figures.

decreases with pressure at constant temperature. A rather successful well-established expression to represent the $\alpha_p(p)$ isotherms was first proposed by Pruzan for n-hexane [8]. This expression is based on a spinodal hypothesis, and can be written in the general form:

$$\alpha_p = \alpha^*(p - p_{sp})^{-1/2}, \tag{1}$$

where p_{sp} is the spinodal pressure and α^* is a proportionality constant which drives the divergence of the thermal expansion coefficient as the spinodal instability is approached. Equation (1) has been used to correlate many experimental data, and its generality has been checked by the present authors [9, 10].

There also exists a general agreement that the isotherms of $\alpha_p(p)$ intersect at high pressures for many liquids, a characteristic feature first described by Bridgman [11]. Authors like Jenner and Millet [5, 6] and Cutler *et al* [12], observed a similar behaviour in complex molecular liquids. A number of recent studies, that will be referred to below, reveal that the crossover of the $\alpha_p(p)$ isotherms seems to be a general property of liquids, as summarized in table 1. A general observation is such intersections usually occur at pressures below 200 MPa. Results for xenon and n-hexane are reproduced in figure 1 as examples.

A number of expressions to account for the temperature dependence of the characteristic parameters in equation (1) have been proposed. Most of them are based on the existence of intersections of the $\alpha_p(p)$ isotherms. For instance, the simplest assumption imposes the existence of a single crossing point. Thus, carbon dioxide and n-butane experimental results were successfully correlated in that way [13]. Later, Polzin and Weiss [14] used this assumption to correlate their experiments in a number of liquids, although the relative narrow range of temperatures covered in their experiments preclude further discussion. The same conclusion can be extracted from our experiments on compressed tetramethylsilane [15] and 2, 3-dimethylbutane [16] using an expansion technique. Table 1 shows that many experimental results cannot be correlated with this simple model, which indicates that a single crossing point criterium is a too restrictive one. As an example, we shall analyse in detail previous results on liquid n-hexane, because this is a well studied substance [17, 18].

Table 1. Liquids studied in this work presenting intersections in $\alpha_p(p)$ isotherms. T_{tp} (K) is the triple point temperature, T_c (K) is the critical temperature, ΔT (K) indicates the range of temperatures where experimental data are available, p_{max} (MPa) is the maximum pressure reached in the experiment, and Δp (MPa) indicates the pressure range where $(\partial\alpha_p/\partial T)_p = 0$. References are listed in the last column.

Liquid	T_{tp}	T_c	ΔT	p_{max}	Δp	References
Argon	83.8	150.8	86–150	320	45–200	[25]
Krypton	115.8	209.4	120–220	373	86–105	[26]
Xenon	161.3	289.74	165–289	385	65–150	[27]
Ethylene	103.97	282.35	110–280	130	43–138	[28]
CF_4	86.4	227.45	95–413	110	75–110	[29]
CHF_3	110.0	299.1	126–332	100	85–101	[30]
CO_2	216.56	304.21	220–304	400	125	[13]
CS_2	161.3	549.4	246–353	400	200	[31]
$Si(CH_3)_4$	182	448.64	198–298	102	60	[15]
n-butane	134.8	425.16	135–425	400	110	[13]
n-hexane	177.8	507.8	238–472	762	36–112	[17, 18]
n-heptane	182.6	540.3	198–310	260	65–140	[32]
2, 3-dimethylbutane	144.6	500.3	208–298	100	40	[33]
Toluene	178.0	591.77	200–480	400	0–148	[23]
Methanol	175.5	512.6	195–305	100	0–80	[24]
Ethanol	158.37	513.9	193–333	280	0–100	[34]
1-hexanol	229.2	610.7	303–503	400	143–405	[35]
m-cresol	285.4	705.8	303–503	400	57–412	[36]
Quinoline	258.0	782.0	303–503	400	58–117	[37]
2, 2, 4-trimethylpentane	165.8	544.0	273–348	200	21	[14]
2, 2-dimethylbutane	173.3	488.8	244–313	200	24	[14]
1, 2-dibromotetrafluoroethane	163.0	487.8	253–369	200	24	[14]
1, 3, 5-trimethylbenzene	228.4	637.3	262–362	200	43	[14]
$Sn(CH_3)_4$	219.2		267–367	200	21	[14]
Pentafluorobenzonitrile	274.8		283–363	200	250	[14]
Cyclohexane	279.6	553.5	293–368	200	22	[14]
Benzene	278.7	562.2	293–352	200	71	[14]

Pruzan [17] fitted his $\alpha_p(p, T)$ measurements in the temperature range 239–472 K to equation (1) using polynomials to account for the temperature variation of α^* and p_{sp}. Randzio *et al* [18] analysed Pruzan's results together with their own α_p experiments between 303 and 503 K using more complex functions for $\alpha^*(T)$ and $p_{sp}(T)$. Although both sets of experiments agree well in (p, V, T) variables, there exist subtle differences in the derived properties which are difficult to resolve in a usual representation of $\alpha_p(p)$ along isotherms (see figure 1). However, these differences are enhanced by plotting $\alpha_p(T)$ along isobaric paths. Thus, from their respective expressions we have calculated the (p, T, α_p) coordinates that obey the condition $(\partial\alpha_p/\partial T)_p = 0$. From their results, this condition yields a minimum in $\alpha_p(T)$ of *n*-hexane. At high temperatures, the minimum shifts to higher pressures with temperature in both cases. However, there exist important discrepancies at low temperatures, as confirmed in figure 2. A further confirmation of this disagreement is observed when the minima conditions are plotted against density instead of temperature, which evidences the necessity of finding an adequate merit function for $\alpha_p(p, T)$ of general applicability.

We have performed a similar analysis for the liquids listed in table 1. These results point to the interesting conclusion that the condition $(\partial\alpha_p/\partial T)_p = 0$ may correspond either to a minimum or a maximum in the α_p isobars, an important issue that merits further discussion.
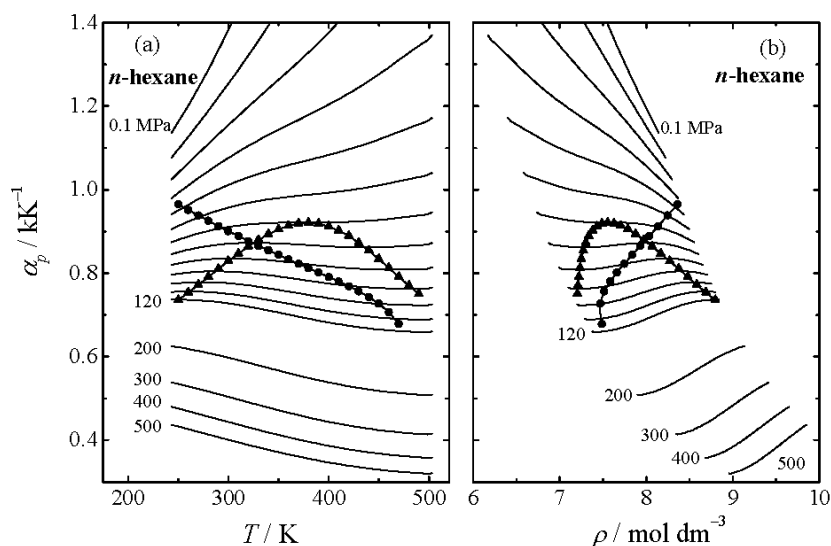
Figure 2. Thermal expansion coefficient of n-hexane plotted against (a) temperature and (b) density. Numbers indicate the following isobaric paths, in MPa: 0.1, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120, 200, 300, 400 and 500 MPa. Curves are data from Randzio et al [18]. Symbols represent the conditions where $(\partial\alpha_p/\partial T)_p = 0$. Triangles have been calculated from data of Randzio et al [18], and circles from the results of Pruzan [17].
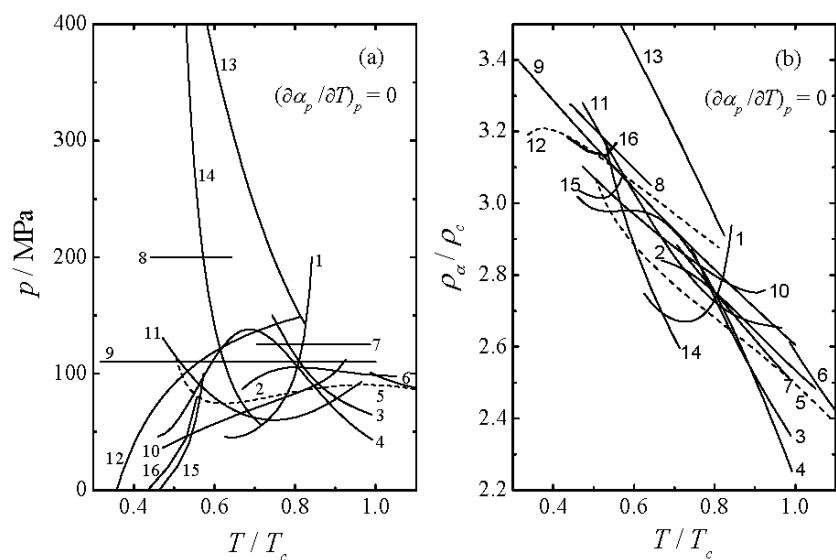

Figure 3. Pressures (a) and reduced densities, (ρ_α/ρ_c) (b) where $(\partial\alpha_p/\partial T)_p = 0$ as functions of reduced temperature (T/T_c) for several liquids: 1: argon [25], 2: krypton [26], 3: xenon [27], 4: ethylene [28], 5: CF_4 [29], 6: CHF_3 [30], 7: carbon dioxide [13], 8: carbon disulfide [31], 9: n-butane [13], 10: n-hexane [17], 11: n-hexane [18], 12: toluene [23], 13: 1-hexanol [35], 14: m-cresol [36], 15: ethanol [34] and 16: methanol [24].

For instance, the intersections in compressed liquid xenon occurs at lower pressures as the temperature increases, so maxima in α_p are found in the stable liquid range, in contrast to the previous example of n-hexane.

Table 2. Pressure ranges (Δp, in MPa) where the condition $(\partial \alpha_p / \partial T)_p = 0$ is fulfilled from several sources. Liquids are grouped together according to the existence of either minima or maxima (or both) along isobaric α_p paths. ΔT_{red} and $\Delta \rho_{red}$ are temperature and density ranges where maxima or minima take place, they are given in reduced units, $T_{red} = T/T_c$ and $\rho_{red} = \rho/\rho_c$, with T_c and ρ_c the critical temperature and density, respectively.

	Minima			Maxima			
Liquid	Δp	ΔT_{red}	$\Delta \rho_{red}$	Δp	ΔT_{red}	$\Delta \rho_{red}$	Reference
Xenon				150–65	0.74–1.00	2.88–2.36	[27]
CHF$_3$				101–85	0.95–1.14	2.61–2.36	[30]
n-heptane				140–65	0.43–0.57	3.45–3.11	[32]
1-hexanol				405–143	0.58–0.82	3.47–2.91	[35]
m-cresol				412–57	0.53–0.71	3.17–2.60	[36]
Argon	45–200	0.65–0.84	2.71–2.94				[25]
n-hexane	36–112	0.47–0.93	3.10–2.76				[17, 18]
Toluene	0–148	0.35–0.81	3.21–2.88				[23]
Methanol	0–80	0.43–0.56	3.18–3.13				[24]
Ethanol	0–100	0.46–0.57	3.04–3.08				[34]
Krypton	86–105	0.67–0.81	2.84–2.74	105–98	0.81–1.05	2.74–2.48	[26]
Ethylene	46–138	0.46–0.69	3.02–2.94	138–43	0.69–0.99	2.94–2.25	[28]

As summarized in table 2, our analysis reveals that there is no apparent correlation between the type of liquid or the pressure range where the extreme condition occurs, although the pressure range where the extrema are found rarely exceeds 100 MPa. In any case, despite this rather erratic behaviour, table 2 allows us to extract some interesting conclusions. In general, the condition $(\partial \alpha_p / \partial T)_p = 0$ always occurs within a relatively narrow range of reduced densities (between 2.2 and 3.5 times the critical density). In addition, the density at the extreme in α_p, ρ_α, always decreases with temperature, except for argon at high temperatures. Furthermore, when minima are found in the α_p isobars, these occur in a very narrow range of density.

The above observations are summarized in figure 3 in reduced variables for all the liquids studied here. It seems clear that there exists no apparent correlation between the pressure at which the condition $(\partial \alpha_p / \partial T)_p = 0$ occurs with other variables like the reduced temperature. However, there exists an evident linear correlation between the reduced densities where that condition is fulfilled and the reduced temperature. This result suggests the existence of a new regularity in the behaviour of liquids not recognized to date, to the best of our knowledge. Although this is not our purpose here, the linear relationship found in figure 3(b) might be used to constrain the temperature and density dependencies of the characteristic parameters of any EOS model intended to represent the (p, V, T) surface of liquids. As mentioned above, we are mainly interested in deriving a general model to reproduce the high-pressure behaviour of the thermal expansion coefficient in an accurate manner. In this regard, the above discussion indicates that a suitable EOS model must satisfy the condition $(\partial \alpha_p / \partial T)_p = 0$ allowing for the presence of both maxima and minima in the α_p isobars. The consequences of this conclusion are discussed in length in the following sections.

2.2. Constraints to an α_p-based thermodynamic model for compressed liquids

In order to analyse the general observations described in the previous section, we shall start examining the temperature derivative of the thermal expansion coefficient in equation (1):

$$\left(\frac{\partial \alpha_p}{\partial T} \right)_p = \alpha_p \left[\frac{1}{\alpha^*} \frac{d\alpha^*}{dT} + \frac{1}{2(p - p_{sp})} \frac{dp_{sp}}{dT} \right]; \qquad (2)$$

hence, the pressure at the extreme condition, $p_{ext}(T)$, is obtained from the condition $(\partial \alpha_p / \partial T)_p = 0$, i.e.,

$$p_{ext}(T) = p_{sp} - \frac{\alpha^*}{2} \frac{\mathrm{d} p_{sp}}{\mathrm{d} T} \left(\frac{\mathrm{d}\alpha^*}{\mathrm{d} T}\right)^{-1} = p_{sp} - \frac{\alpha^*}{2} \left(\frac{\mathrm{d}\alpha^*}{\mathrm{d} p_{sp}}\right)^{-1}, \tag{3}$$

since both α^* and p_{sp} depend only on temperature.

This formulation has the advantage that the dependence on temperature is included through $p_{sp}(T)$, which has a well-known temperature behaviour [19, 20]. Thus, our model requires a merit function to represent $p_{sp}(T)$. We shall make use of the proved relationship between p_{sp} and surface tension [19, 21] to provide a suitable simple expression. Reid *et al* [2] compiled a series of functional forms to account for the temperature dependence of surface tension. An accurate expression that has proved successful in representing extensive experimental data [22] is the following,

$$p_{sp}(T) = p_{vap}(T) + p^* \left[\frac{(1 - T/T_C)^{3\varepsilon}}{T/T_C}\right]^{1/2}, \tag{4}$$

where T_C stands for the critical temperature and p^* is an scaling pressure. The first term, p_{vap}, is the vapour pressure that is only important at temperatures very close to T_C. Although equation (4) is similar to other previously reported [2, 22], it has been modified to include the explicit dependence on the scaling pressure p^*. Thus, in the following discussion it is important to bear in mind that the spinodal pressure typically increases with temperature up to the critical point. There are a few exceptions, like water, that show an uncommon reentrant behaviour at low temperatures [16].

From equation (3), taking the second derivative of α_p with respect to temperature, we obtain,

$$\left(\frac{\partial^2 \alpha_p}{\partial T^2}\right)_p (p_{ext}, T) = \frac{1}{[p_{ext} - p_{sp}]^{1/2}} \left\{\frac{\mathrm{d}^2\alpha^*}{\mathrm{d} T^2} + \frac{1}{\alpha^*}\left(\frac{\mathrm{d}\alpha^*}{\mathrm{d} T}\right)^2 - \frac{\mathrm{d}\alpha^*}{\mathrm{d} p_{sp}}\frac{\mathrm{d}^2 p_{sp}}{\mathrm{d} T^2}\right\}$$

$$= \frac{1}{[p_{ext} - p_{sp}]^{1/2}} \left(\frac{\mathrm{d} p_{sp}}{\mathrm{d} T}\right)^2 \left[\frac{\mathrm{d}^2\alpha^*}{\mathrm{d} p_{sp}^2} + \frac{1}{\alpha^*}\left(\frac{\mathrm{d}\alpha^*}{\mathrm{d} p_{sp}}\right)^2\right]. \tag{5}$$

We have found that α^* always decreases with p_{sp} for all the liquids studied here, so the sign on the second derivative of α_p with temperature is driven by the first term into brackets. Thus, if $(\mathrm{d}^2\alpha^*/\mathrm{d} p_{sp}^2)$ is positive, only minima are found in the α_p isobars, while if $(\mathrm{d}^2\alpha^*/\mathrm{d} p_{sp}^2)$ is negative, both maxima and minima can occur. This observation allows us to examine in terms of equation (5) the suitability of the previous models proposed to represent $\alpha_p(p, T)$. We will not consider polynomials like those proposed by Pruzan [17] and Randzio [18] because their empirical nature.

One of the first expressions proposed in the literature to describe the behaviour of $\alpha_p(p, T)$ in compressed liquids is that due to Alba *et al* [13],

$$\alpha^*(T) = \alpha_0 [p_0 - p_{sp}(T)]^{0.5}, \tag{6}$$

which is a convex function on the temperature. This expression was derived assuming that (α_0, p_0) represent the coordinates of a single crossing point for the α_p isotherms of a liquid, its generality is therefore rather limited. Ter Minassian *et al* [23] modified equation (6) to correlate their experimental α_p for liquid toluene using the following expression:

$$\alpha^*(T) = \alpha_0 [p_0 - p_{sp}(T)]^2, \tag{7}$$

where α_0 and p_0 do not define a single crossing point, but are only adjustable parameters. The first and second derivatives with respect to p_{sp} are,

$$\frac{\mathrm{d}\alpha^*}{\mathrm{d} p_{sp}} = -2\alpha_0 [p_0 - p_{sp}(T)] \qquad \text{and} \qquad \frac{\mathrm{d}^2\alpha^*}{\mathrm{d} p_{sp}^2} = 2\alpha_0. \tag{8}$$

Table 3. Curvature of $\alpha^*(p_{sp})$ and conditions for an α_p extrema as a function of the parameter ω in equation (10).

ω	$(d^2\alpha^*/dp_{sp}^2)$	$\alpha^*(p_{sp})$	Temperature range	$(\partial^2\alpha_p/\partial T^2)_p$	Extrema
$0 < \omega \leqslant 0.5$	<0	Convex	T_{tp}–T_c	<0	Maxima
$0.5 < \omega < 1$	<0	Convex	$T_{tp} < T$	>0	Minima
			$T < T_c$	<0	Maxima
$\geqslant 1$	>0	Concave	T_{tp}–T_c	>0	Minima

Since α_0 is defined positive, the algebraic form of equation (7) imposes that the α_p isobars must exhibit only minima (the intersections between isotherms are displaced to higher pressures with increasing temperature), which again disagrees with our general findings. This is readily confirmed from the corresponding expression for $p_{ext}(T)$:

$$p_{ext}(T) = \frac{[p_0 + 3p_{sp}(T)]}{4}, \tag{9}$$

by noting that $p_{sp}(T)$ is an increasing function of the temperature.

2.3. An α_p-based thermodynamic model for compressed liquids

In order to derive a general thermodynamic model for compressed liquids, we will consider the following expression for $\alpha^*(p_{sp})$,

$$\alpha^*(T) = \alpha_0^*\left[1 + A\left(\frac{p_{sp}(T) - p_c}{p^*}\right)^\omega\right]. \tag{10}$$

This model depends on four parameters: α_0^*, A, p^*, and ω, which are always positive, except p^* and p_c is the critical pressure of the substance. α_0^* is the value of α^* at critical conditions, and p^* is the scaling parameter for the spinodal pressure in equation (4). The relevant parameter in equation (10) is the exponent ω that determines the curvature of $\alpha^*(T)$. Thus, from equations (5) and (10) it follows that the condition that determines the change in sign of $(\partial^2\alpha_p/\partial T^2)_p$ is:

$$A\left[\frac{p_{sp} - p_c}{p^*}\right]^\omega = \frac{1 - \omega}{2\omega - 1}. \tag{11}$$

Since the left-hand term in equation (11) is always positive, we may rationalize the behaviour of $\alpha_p(T)$ only in terms of ω; there are three different scenarios, which are summarized in table 3. Now, the pressure at the extreme condition, $p_{ext}(T)$, can be calculated from:

$$p_{ext}(T) = p_{sp}(T) - \frac{[p_{sp}(T) - p_c]}{2\omega}\left[1 + \frac{1}{A}\left(\frac{p_{sp}(T) - p_c}{p^*}\right)^{-\omega}\right], \tag{12}$$

which may correspond to both maxima or minima in $\alpha_p(T)$.

The α_p-based EOS is therefore expressed by equations (1), (4) and (10), and it depends only on five parameters: $p^*, \varepsilon, \alpha_0^*, A$ and ω. We have correlated available experimental data of $\alpha_p(p, T)$ to equations (1), (4) and (10) for a number of liquids. The characteristic parameters for several liquids are listed in table 4, together with absolute standard deviations of the fit from experimental values of $\alpha_p(p, T)$. An interesting result is that the parameter A can be fixed to unity without loss of accuracy for those experiments correlated using equations (6) and (7). In such a case, our model fits the experimental data with a comparable quality using the same number of characteristic parameters. In addition, we have found that the exponent ε
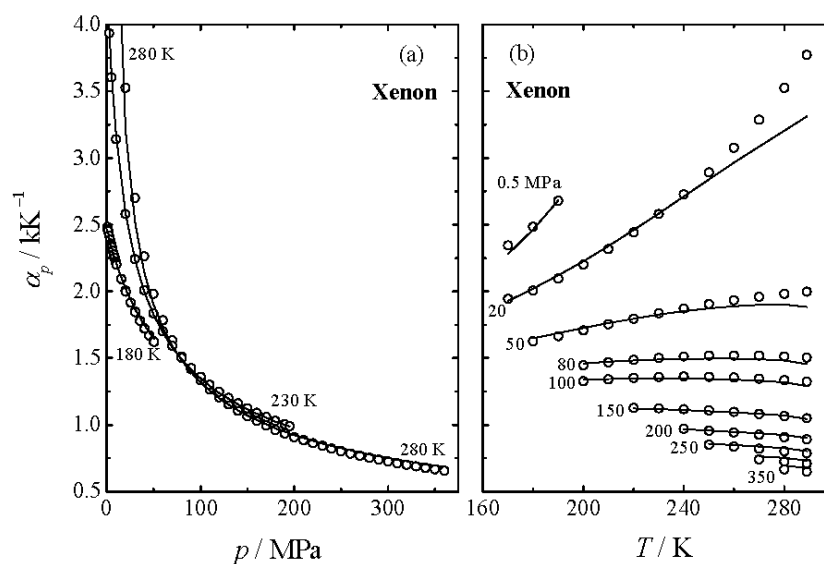
Figure 4. Thermal expansion coefficient of liquid xenon along (a) isothermal and (b) isobaric paths. Symbols are experimental results taken from Streett *et al* [27]. Curves are results calculated from our model using the characteristic parameters listed in table 4 and $T_c = 289.74$ K.

Table 4. Characteristic parameters of our $\alpha_p(p, T)$ model (equations (1), (4) and (10)). Standard deviations (SD) from experimental data are listed on the last column.

Liquid	References	p^*(MPa)	3ε	α_0^*(MPa$^{0.5}$ kK^{-1})	A	ω	SD(kK^{-1})
Argon	[25]	-170.6 ± 10.4	3.90 ± 0.09	23.10 ± 0.03	2.70 ± 0.44	1.74 ± 0.06	0.05
Krypton	[26]	-203.8 ± 7.0	3.91 ± 0.05	17.25 ± 0.04	0.95 ± 0.08	0.94 ± 0.03	0.06
Xenon	[27]	-207.7 ± 4.7	3.89 ± 0.03	12.42 ± 0.03	0.63 ± 0.02	0.59 ± 0.02	0.08
Ethylene	[28]	-181.5 ± 3.4	3.58 ± 0.03	13.56 ± 0.02	0.83 ± 0.02	0.95 ± 0.01	0.04
CF$_4$	[29]	-135.6 ± 3.6	3.26 ± 0.04	16.12 ± 0.03	0.58 ± 0.02	0.86 ± 0.02	0.08
Si(CH$_3$)$_4$	[15]	-122.5 ± 5.8	3.05 ± 0.11	6.04 ± 0.76	1.14 ± 0.25	0.57 ± 0.10	0.01
2, 3-dimethyl- butane	[33]	-207.6 ± 13.8	4.16 ± 0.18	4.46 ± 0.78	2.23 ± 0.53	0.57 ± 0.08	0.01
Toluene	[23]	-220.6 ± 2.6	3.48 ± 0.02	7.42 ± 0.01	0.85 ± 0.01	1.26 ± 0.01	0.01
Methanol	[24]	-140.7 ± 6.9	2.01 ± 0.14	8.85 ± 0.26	0.46 ± 0.08	1.16 ± 0.04	0.01
n-hexane	[17]	-201.6 ± 1.7	3.65 ± 0.01	6.89 ± 0.02	1	0.78 ± 0.01	0.05
n-hexane	[18]	-200.3 ± 1.5	3.64 ± 0.01	6.97 ± 0.01	1	0.79 ± 0.01	0.05
1-hexanol	[35]	-205.7 ± 6.7	2.92 ± 0.06	4.86 ± 0.03	1	0.18 ± 0.01	0.01
m-cresol	[36]	-190.4 ± 11.4	2.31 ± 0.12	5.29 ± 0.09	1	0.50 ± 0.02	0.01
Quinoline	[37]	-214.5 ± 12.9	2.95 ± 0.15	5.42 ± 0.16	1	0.89 ± 0.05	0.01

is close to unity for all the liquids studied. This result confirms the physical meaning of the characteristic parameters included in our model, as concluded from previous surface tension correlation schemes [2, 21, 22].

A comparison of the quality of our model to account for both temperature and pressure variations of $\alpha_p(p, T)$ is illustrated in figure 4 for xenon over the whole liquid range. The global agreement with the experiment is quite remarkable, especially along the isobaric paths. Deviations are observed only in the vicinity of the critical point due to the expected divergence of α_p as the critical point (which is the only stable point of the spinodal curve) is approached.

3. Conclusion

We have analysed the general behaviour of the thermal expansion coefficient, α_p, as a function of pressure and temperature for a number of liquids. Our analysis suggests that the condition that the isotherms of α_p present intersections at high pressure is not sufficient to derive thermodynamic models for compressed liquids of general applicability, as previously suggested. We therefore conclude that the relevant information concerns whether the intersections of the $\alpha_p(p)$ isotherms shift with temperature or not, and in which direction. On this basis, existing models for $\alpha_p(p, T)$ have been criticized, and we have proposed an α_p-based model that meets the desired features. Our model depends only on five parameters. The number of adjustable parameters can be reduced to three by fixing to unity both A and ε in our correlation scheme when experimental data are available in narrow ranges of temperatures.

Finally, we must emphasize that our model is applicable to any liquid showing the typical behaviour of $\alpha_p(T)$ at room pressure, namely, to increase with temperature. Of course, there are well-known exceptions to this rule. Besides water, other liquids like toluene [23] or methanol [24] exhibit minima in α_p at temperatures close to the solidification line. For these liquids specific merit functions for the temperature dependence of the characteristic parameters in equation (1) are required to acquire quantitative results at low temperatures.

Acknowledgment

References

[1] Macdonald J R 1969 *Rev. Mod. Phys.* **40** 316
[2] Reid R C, Prausnitz J M and Sherwood T K 1977 *The Properties of Gases and Liquids* 3rd edn (New York: McGraw-Hill)
[3] Tekác V, Cibulka I and Holub R 1985 *Fluid Phase Equilib.* **19** 33
[4] Randzio S L and Deiters U K 1995 *Ber. Bunsenges. Phys. Chem.* **99** 1179
[5] Jenner G and Millet M 1970 *High Temp.–High Pressure* **2** 205
[6] Jenner G and Millet M 1973 *High Temp.–High Pressure* **5** 145
[7] Randzio S L 1986 *Phys. Lett.* A **117** 473
[8] Pruzan Ph 1984 *J. Phys. Lett.* **45** L273
[9] Baonza V G, Cáceres M and Núñez J 1993 *Chem. Phys. Lett.* **216** 553
[10] Baonza V G, Cáceres M and Núñez J 1993 *J. Phys. Chem.* **97** 10813
[11] Bridgman P W 1970 *The Physics of High Pressure* (New York: Dover)
[12] Cutler W G, McMickle R H, Webb W and Schiessler R W 1958 *J. Chem. Phys.* **29** 727
[13] Alba C, Ter Minassian L, Denis A and Soulard A 1985 *J. Chem. Phys.* **82** 384
[14] Polzin B and Weiss A 1990 *Ber. Bunsenges. Phys. Chem.* **94** 746
[15] Baonza V G, Cáceres M and Núñez J 1989 *J. Chem. Thermodyn.* **21** 1045
[16] Baonza V G, Cáceres M and Núñez J 1994 *J. Phys. Chem.* **98** 1993
[17] Pruzan Ph 1991 *J. Chem. Thermodyn.* **23** 247
[18] Randzio S L, Grolier J-P E, Quint J R, Eatough D J, Lewis E A and Hansen L D 1994 *Int. J. Thermophys.* **15** 415
[19] Skripov V P 1974 *Metastable Liquids* (New York: Wiley)
[20] Debenedetti P G 1996 *Metastable Liquids: Concepts and Principles* (Princeton, NJ: Princeton University Press)
[21] Rubio J E F, Baonza V G, Cáceres M and Núñez J 1994 *Ber. Bunsenges. Phys. Chem.* **98** 960
[22] Jasper J J 1972 *J. Phys. Chem. Ref. Data* **1** 841
[23] Ter Minassian L, Bouzar K and Alba C 1988 *J. Phys. Chem.* **92** 487
[24] Taravillo M 1999 *PhD Thesis* Universidad Complutense de Madrid
[25] Streett W B 1974 *Physica* **76** 59
[26] Streett W B and Staveley L A K 1971 *J. Chem. Phys.* **55** 2495

[27] Streett W B, Sagan L S and Staveley L A K 1973 *J. Chem. Thermodyn.* **5** 633

[28] Calado J C G, Clancy P, Heintz A and Streett W B 1982 *J. Chem. Eng. Data* **27** 376

[29] Rubio R G, Calado J C G, Clancy P and Streett W B 1985 *J. Phys. Chem.* **89** 4637

[30] Rubio R G, Zollweg J A and Streett W B 1989 *Ber. Bunsenges. Phys. Chem.* **93** 791
      Rubio R G, Zollweg J A, Polanco J M G, Calado J C G, Miller J and Streett W B 1991 *J. Chem. Eng. Data* **36**
            171

[31] Tomaszkiewicz I and Ter Minassian L 1988 *J. Phys. Chem.* **92** 6824

[32] Muringer M J P, Trappeniers N J and Biswas S N 1985 *Phys. Chem. Liq.* **14** 273
      Sun T F, Bominaar S A R C, Ten Seldam C A and Biswas S N 1991 *Ber. Bunsenges. Phys. Chem.* **95** 696

[33] Baonza V G, Cáceres M and Núñez J 1993 *J. Phys. Chem.* **97** 2002

[34] Sun T F, Ten Seldam C A, Kortbeek P J, Trappeniers N J and Biswas S N 1988 *Phys. Chem. Liq.* **18** 107
      Sun T F, Schouten J A and Biswas S N 1991 *Int. J. Thermophys.* **12** 381

[35] Randzio S L, Grolier J-P E and Quint J R 1995 *Fluid Phase Equilib.* **110** 341

[36] Randzio S L, Lewis E A, Eatough D J and Hansen L D 1995 *Int. J. Thermophys.* **16** 883

[37] Randzio S L, Eatough D J, Lewis E A and Hansen L D 1996 *Int. J. Thermophys.* **17** 405