



Transition in fluctuation behaviour of normal liquids under high pressures



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HIGHLIGHTS

- There are two regions with the different fluctuation behaviour.
- Fluctuation transition is determined by the random loose/close packing.
- The crossing of expansivity isotherms coincides with this transition.

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ABSTRACT

We explore the behaviour of the inverse reduced density fluctuations and the isobaric expansion coefficient using α , ω -dibromoalkanes as an example. Two different states are revealed far from the critical point: the region of exponentially decaying fluctuations near the coexistence curve and the state with longer correlations under sufficiently high pressures. The crossing of the isotherms of the isobaric expansion coefficient occurs within the PVT range of the mentioned transition. We discuss the interplay of this crossing with the changes in molecular packing structure connected with the analysed function of the density, which represents inverse reduced volume fluctuations.

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1. Introduction

The isobaric coefficient of thermal expansion is a thermoelastic property defined as $\alpha_p \equiv -\rho^{-1}(\partial\rho/\partial T)_p$ and related to the thermal response of the system. This definition of the expansion coefficient refers both to a solid and a liquid phase. While the theory of the thermal expansion of solids is well developed and it is known that the thermal expansion in solid condensed systems is mainly caused by the anharmonicity of oscillations [1], in the case of liquids, the understanding of this thermodynamic function in terms of molecular behaviour is still a challenge.

Extremely interesting is that the pressure dependence of the isotherms of thermal expansivity can exhibit anomalous behaviour in the case of simple liquids, i.e. isotherms present crossing in some characteristic pressure range, in which $(\partial\alpha_p/\partial T)_p = 0$. Although the first observation of this phenomenon is dated to the work by P.G. Bridgman [2], its comprehensive studies have been evaluated during the last decades only [3–9]. The curve, at which the derivative with respect to temperature vanishes, divides the $p - T$ plane into two regions where $(\partial\alpha_p/\partial T)_p > 0$ and $(\partial\alpha_p/\partial T)_p < 0$. The latter corresponds to the anomalous volume expansion response to the increasing temperature.

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Some single-phase equations of state, which can reproduce such a behaviour, as a rule postulate this crossing *a priori* and introduce several adjustments to this fact, as the modified repulsive contribution to the Carnahan–Starling model [10], the shifted Lennard-Jones pair potentials [11] or the spinodal hypothesis [5,12–14].

In our study, we consider the isothermal equation of state based on the continuation of the fluctuation law detected for a saturated liquid into the single-phase region. This approach results in the crossing of the thermal expansivity isotherms without any additional assumptions. As well, we discuss its background from the point of view of liquid structure characteristics.

2. The crossing of expansivity isotherms and molecular packing

The fluctuation model is based on the consideration of the inverse magnitude of reduced volume fluctuations. This quantity is determined as an inverse ratio of relative volume fluctuations in a condensed medium to their value for the hypothetical ideal gas at the same PVT thermodynamic conditions:

$$v = \left[\frac{\langle (\Delta V)^2 \rangle}{V} / \frac{\langle (\Delta V)_{ig}^2 \rangle}{V_{ig}} \right]^{-1} = \frac{\mu_0}{RT} [\rho \beta_T]^{-1}, \quad (1)$$

where μ_0 , R , T , ρ , β_T are the molar mass, the gas constant, the temperature, the mass density and the isothermal compressibility correspondingly.

It has been observed [15] that this parameter for simple real liquids and the model lattice fluid has the exponential dependence on the density

$$v = \exp(\kappa \rho + b) \quad (2)$$

along the coexistence curve well below the critical point curve. The coefficients κ , b have a very weak dependence on the temperature and could be considered as constants with a reasonable accuracy [15–17].

The assumption of the same functional dependence within the single-phase region of liquids taken under elevated pressure allows for a simple integration of Eq. (1) with the substituted (2). This procedure results in the two-parametric Fluctuation-based Tait-like isothermal Equation of State (FT-EoS)

$$\rho = \rho_0 + \frac{1}{\kappa} \log \left[\frac{\kappa \mu_0}{v(\rho_0)RT} (P - P_0) + 1 \right], \quad (3)$$

which can be used for a prediction of the density along an isotherm [16]. Its further differentiation with respect to the temperature provides the expression for the isobaric expansion coefficient [17]

$$\alpha_p = \alpha_p^0 \frac{\rho_0}{\rho} e^{-\kappa(\rho - \rho_0)} + \frac{1 - e^{-\kappa(\rho - \rho_0)}}{\kappa \rho T}. \quad (4)$$

Here in (3) and (4) the index 0 marks the values taken at the referent state: the data taken along the coexistence curve or at the normal pressure well below the critical point.

Now let us show that the properties of Eq. (4) imply an existence of the crossing $(\partial \alpha_p / \partial T)_p = 0$ without any artificial assumptions. The derivative of α_p defined by Eq. (4) with respect to the temperature at a constant pressure gives

$$\left(\frac{\partial \alpha_p}{\partial T} \right)_p = \alpha_p^2 + \frac{1}{\rho} \left\{ -\frac{1}{\kappa T^2} + \left[\rho_0 \left(\left(\frac{\partial \alpha_p^0}{\partial T} \right)_p - \alpha_p^{02} \right) + \frac{1}{\kappa T^2} + \kappa \left(\rho_0 \alpha_p^0 - \frac{1}{\kappa T} \right) (\rho \alpha_p - \rho_0 \alpha_p^0) \right] e^{-\kappa(\rho - \rho_0)} \right\}. \quad (5)$$

For $\rho = \rho_0$ it reduces to $(\partial \alpha_p^0 / \partial T)_p > 0$. At the high-density asymptotics $\rho \gg \rho_0$, the exponential factor multiplied by the square bracket in (5) tends to zero and the rest terms,

$$\left(\frac{\partial \alpha_p}{\partial T} \right)_p = \alpha_p^2 - \frac{1}{\rho \kappa T^2} < 0 \quad (6)$$

taking into account the characteristic orders of the included thermodynamic values for the studied organic liquids such as n-alkanes and their halogenated.

Rather, Eq. (6) provides an opportunity to check whether or not the crossing occurs based on the saturated data for α_p and ρ of the compressed liquid calculated from Eq. (3) (or some other well-established isothermal approximation, say the classical Tait equation with known coefficients).

However, Eq. (6) is a crude estimator, which indicates the fact of existence (or nonexistence). The practical calculation of the proper density region requires an application of the full formula (5) with the substituted density determined by Eq. (3) under the given elevated pressure P . It should be also noted that Eq. (5) is the point-wise one with respect to the temperature, i.e. it implies the calculation along a single isotherm if the referent α_p is known.

The present model was tested using experimental data concerning the density, the speed of sound and the thermal expansivity of α , ω -dibromoalkanes (1, 3-dibromopropane to 1, 6-dibromohexane [17], dibromomethane [18], and the

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