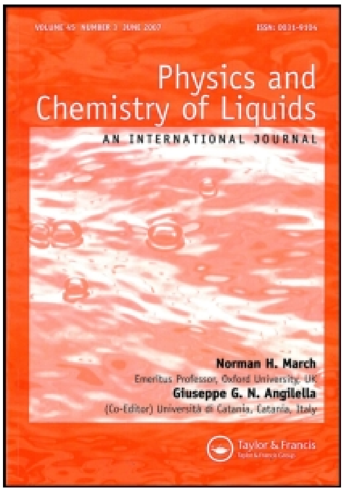

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On some thermophysical properties of alkanes along the liquid–vapour coexistence line and the corresponding states principle

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The Grüneisen thermodynamic parameter, the internal pressure and the long wavelength limit of the static structure factor have been evaluated from basic thermal quantities (pressure, density or volume, heat capacities at constant pressure and volume and sound velocity) using only exact thermodynamic relations for the complete sequence of *n*-alkanes ($n = 1$–24) along the liquid–vapour coexistence line. A common behaviour has been observed in accordance with the corresponding states principle. Expressions depending on reduced temperature and the chain length have been obtained for these quantities fitting very well the values assigned to the quantities aforementioned.

Keywords: Alkane; Corresponding states principle; Grüneisen's parameter; Internal pressure; Static structure factor

1. Introduction

The evaluation and correlation of thermophysical properties is a matter of great interest in the fields of chemistry, chemical engineering, physics and materials science.

Laboratories of repute and many scientists have provided a large number and variety of experimental measurements, criteria for their evaluation and extensive tables for the more important quantities.

In the context of equilibrium thermodynamics these properties are temperature, pressure, density (or volume), energy, enthalpy, entropy, heat capacities at constant pressure and volume and sound velocity. If one extends the scope to transport properties, viscosity and thermal conductivity coefficients are also to be included. The researchers will thus attempt to interpret them in the most general terms possible.

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An important tool in this field is that of the corresponding states principle (CSP). This hypothesis, originally advanced by van der Waals, postulates that thermodynamic properties of fluids obey two-parameter universal equations when reduced by their critical constants or equivalent parameters. This is indeed a good approximation for simple fluids (Ar, Kr, Xe and CH_4). The critical temperature and critical pressure are the two characteristic parameters of a corresponding-states method. Pitzer pointed out that by including a third parameter for each substance, the corresponding states approximation can be extended to other fluids [1,2]. Any two substances having the same value of this parameter can then be regarded as having the same thermodynamic properties. This parameter, called acentric factor w, is given in terms of the reduced vapour pressure $P_r = P/P_c$ at a reduced temperature of $T_r = T/T_c = 0.7$; thus

$$w = -\log P_r - 1 \tag{1}$$

In other words, in van der Waals's picture, the equation of state can be written in the form:

$$f(P_r, V_r, T_r) = 0 \tag{2}$$

whereas in Pitzer's picture, we write:

$$f(P_r, V_r, T_r, w) = 0 \tag{3}$$

instead of equation (2).

Extension of the CSP to polar fluids involves the addition of a fourth parameter to account for polarity effects. The reduced dipole moment seems the most suitable choice given that this quantity is a fundamental electric property of the molecule.

In order to obtain an analytical representation of the Pitzer method suitable for digital computation, Lee and Kesler [3] reformulated the three-parameter corresponding states. In this form, the theory is applicable only to nonpolar fluids. However, a more general form [4] using two reference fluids can be applied to a wider range of fluids, including those exhibiting polarity. This form is called the extended corresponding-states principle (ECSP).

Recently the CSP has shown an important revival reinforcing its microscopic background [5,6] and the ECSP has extended its field of application to mixtures [7] and prediction of volumetric properties [8].

In this work, we have extended the study to the following quantities: Grüneisen's thermodynamic parameter, internal pressure and static structure factor at the long-wavelength limit along the liquid–vapour coexistence line. To the best of our knowledge, the principle has not been tested previously for these cases. Its verification therefore represents an important advance.

Except for the internal pressure, the remaining quantities are adimensional and so the scaling is unnecessary.

We have chosen the sequence of n-alkanes ($n = 1$–24) for this study.

2. Theory

The data used in this analysis have been the quantities cited before. Their numerical values were taken from the bibliography [9,10].

First, we have to deduce the appropriate relations.

2.1. *Grüneisen's thermodynamic parameter*

From an adequate model of solid, Grüneisen [11] proposed the following equation of state:

$$PV + g(V) = \Gamma U \tag{4}$$

where Γ is Grüneisen's parameter or constant, $g(V)$ depends only on volume and U is the internal energy.

It is easily shown that

$$\Gamma = \frac{\alpha V}{\beta_{\mathrm{T}} C_{\mathrm{V}}} = \frac{\alpha V}{\beta_{\mathrm{S}} C_{\mathrm{P}}} = \frac{\alpha M u^2}{C_{\mathrm{P}}} \tag{5}$$

where α is the volume expansion coefficient, β_{T} and β_{S} are the isothermal and adiabatic compressibility coefficients, M is the molecular mass and u is the velocity of sound. As

$$\alpha = \left[\frac{C_{\mathrm{P}}}{MTu^2}\left(\frac{C_{\mathrm{P}}}{C_{\mathrm{V}}} - 1\right)\right]^{1/2} \tag{6}$$

substituting this into (5), we obtain

$$\Gamma = \left[\frac{C_{\mathrm{P}}}{\rho u^2 C_{\mathrm{V}}}\frac{(C_{\mathrm{P}} - C_{\mathrm{V}})\rho}{MT}\right]^{1/2}\frac{Mu^2}{C_{\mathrm{P}}} = \left[\left(\frac{1}{C_{\mathrm{V}}} - \frac{1}{C_{\mathrm{P}}}\right)\frac{M}{T}\right]^{1/2} u \tag{7}$$

Several researchers [12,13] have transferred their meaning to liquids without substantial variations.

2.2. *Internal pressure*

This quantity is defined thermodynamically as

$$P_i = \left(\frac{\partial U}{\partial V}\right)_{\mathrm{T}} = T\left(\frac{\partial P}{\partial T}\right)_{\mathrm{V}} - P = T\frac{\alpha}{\beta_{\mathrm{T}}} - P \tag{8}$$

and plays an essential role, owing to the close relation with the cohesive energy density of the matter. Complete information about this quantity with a brief bibliography can be found in an excellent review article [14].

As

$$\beta_{\mathrm{T}} = \frac{C_{\mathrm{P}} V}{Mu^2 C_{\mathrm{V}}} \tag{9}$$

then

$$P_i = \frac{u}{V}\left[MTC_{\mathrm{V}}\left(1 - \frac{C_{\mathrm{V}}}{C_{\mathrm{P}}}\right)\right]^{1/2} - P \tag{10}$$

Obviously this quantity can be connected with the Grüneisen's parameter eliminating some of the basic quantities. This relation is written as

$$P_i = \frac{C_V T \Gamma}{V} - P \tag{11}$$

2.3. *The static structure factor at high wavelength*

The static structure factor is crucial for determining the structure of a substance. For liquids it has an additional significance owing to its relation with the radial distribution function [15].

From the Ornstein–Zernike relation [16]

$$\beta_T = \frac{1}{nkT} \lim_{Q \to 0} S(Q) \tag{12}$$

where Q is the wave number and $S(Q)$ is the static structure factor.

Therefore, its value for the long wavelength limit is

$$S(0) = nkT\beta_T = \frac{N}{V} kT\beta_T = \frac{RT}{V}\beta_T = \frac{\beta_T}{\beta_{id}} \quad \text{where } \beta_{id} = \frac{1}{P} = \frac{V}{RT} \tag{13}$$

Substituting the earlier expression for β_T, we obtain

$$S(0) = \frac{C_P RT}{C_V M u^2} \tag{14}$$

It is also possible to relate directly $S(0)$ with Γ and P_i by means of the following expressions

$$\Gamma = \left[\frac{(C_P/C_V) - 1}{C_V} \frac{R}{S(0)} \right]^{1/2} \tag{15}$$

$$P_i = \frac{T}{V}\left[(C_P - C_V) \frac{R}{S(0)} \right]^{1/2} - 1 \tag{16}$$

3. Results and discussion

Grüneisen's parameter has been evaluated from (7) for all n-alkanes ($n = 1$–24). Figures 1–3 show the results for low ($n = 1$–8), intermediate ($n = 9$–16) and high ($n = 17$–24) alkanes, this quantity being plotted against the reduced temperature T_r.

Generally Grüneisen's parameter decreases with the molar mass. It is easily explained because the anharmonic effects increase. The same reason justifies that this quantity always decreases with the temperature.

Higher differences can be observed for low alkanes. Even the curvature is distinct for methane and ethane with respect to the rest.

On the other hand, the differences are small for the other two groups. The values almost coincide for $T_r > 0.6$.

For each individual alkane, an exponential decay $\Gamma = ae^{-bTr}$ reproduces the results very well except for methane and ethane.

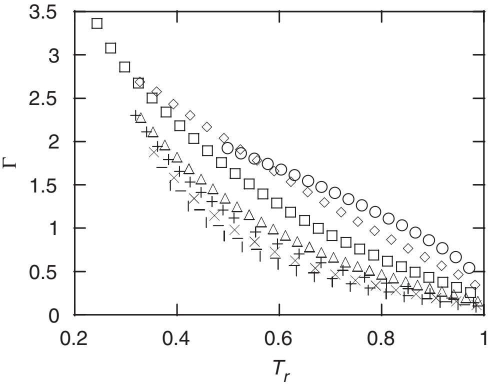

Figure 1. Variation of Grüneisen's parameter Γ with the reduced temperature T_r for lower *n*-alkanes. Points: $n = 1$ (○); $n = 2$ (◇); $n = 3$ (□); $n = 4$ (Δ); $n = 5$ (+); $n = 6$ (×); $n = 7$ (–); $n = 8$ (|).

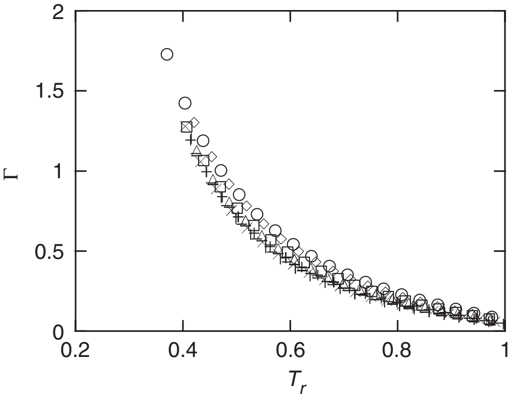

Figure 2. As in figure 1 for intermediate *n*-alkanes. Points: $n = 9$ (○); $n = 10$ (◇); $n = 11$ (□); $n = 12$ (Δ); $n = 13$ (+); $n = 14$ (×); $n = 15$ (–); $n = 16$ (|).

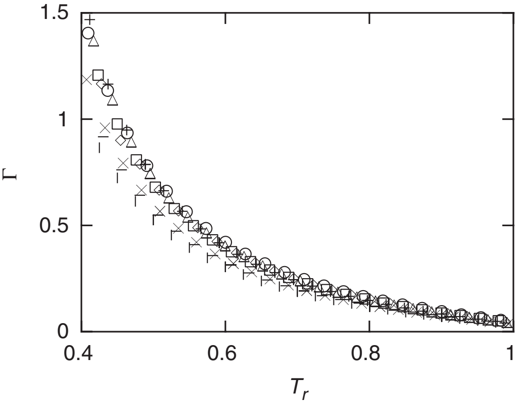

Figure 3. As in figure 1 for higher *n*-alkanes. Points: $n = 17$ (○); $n = 18$ (◇); $n = 19$ (□); $n = 20$ (Δ); $n = 21$ (+); $n = 22$ (×); $n = 23$ (–); $n = 24$ (|).

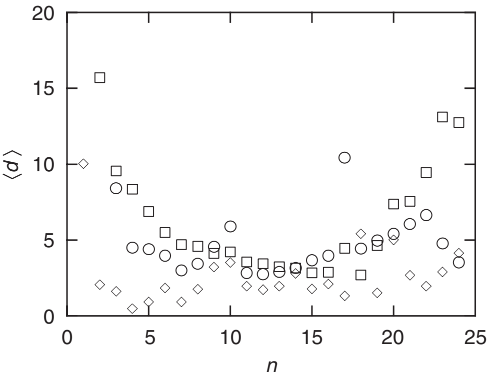

Figure 4. Mean deviation $\langle d\rangle$ for Grüneisen's parameter Γ(○), reduced internal pressure P_{ir} (◇) and static structure factor at high wavelength $S(0)$ (□) with the chain length n of the alkane.

Such results suggest a common behaviour in accordance with the CSP. In other words, the family of curves can be represented by such a relation if a and b depend on an additional parameter. If this is the acentric factor, the agreement is not good. Furthermore, the values of this quantity present a considerable incertitude for higher n-alkanes. The correlation improves substantially by substituting the acentric factor for the chain length n.

Both parameters can be expressed adequately by the following formulas:

$$a = 5.5108 + 1.5793n - 0.27652n^2 + 0.018674n^3 - 0.00040838n^4 \tag{17}$$

$$b = 1.3167 + 0.90765n - 0.098494n^2 + 0.050431n^3 - 9.3519 \times 10^{-5}n^4 \tag{18}$$

For each point involved, we introduce the percentage relative deviation

$$d(\%) = 100\frac{\left|\Gamma_{\text{exp}} - \Gamma_{\text{calc}}\right|}{\Gamma_{\text{exp}}} \tag{19}$$

An upper limit $T_r < 0.95$ has been taken in order to present it being too close to the critical point. We have then 437 points, corresponding 16 at least to each alkane.

The mean deviation $\langle d\rangle$ for each alkane is the mean value of this quantity over the points corresponding to this substance.

Figure 4 shows the results obtained with this procedure. The lower alkanes (methane and ethane) have been suppressed for the reasons above mentioned. The remaining points present a deviation less than 10% and those lower than 5% are predominant. The mean deviation for all alkanes is 4.8%.

Internal pressure has been evaluated for all n-alkanes. Figures 5–7 show the results for the three groups where the reduced internal pressure $P_{ir} = P_i/P_c$ is plotted against the reduced temperature T_r.

This quantity increases with the molar mass because the effects of molecular complexity play an opposing role with regard to Grüneisen's parameter. However P_i varies against T_r as Γ, in accordance with (11).

Also here the values of P_{ir} tend to coincide although for a higher value in relation to the preceding case.

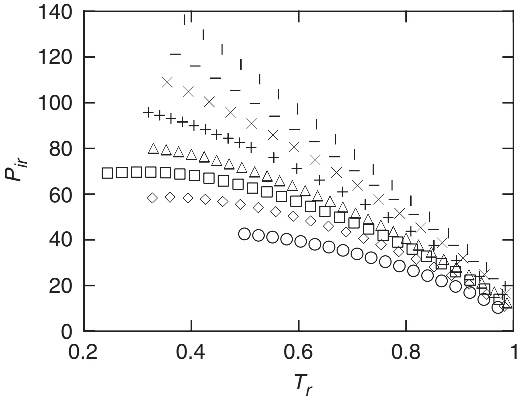

Figure 5. As in figure 1 for reduced internal pressure P_{ir}.

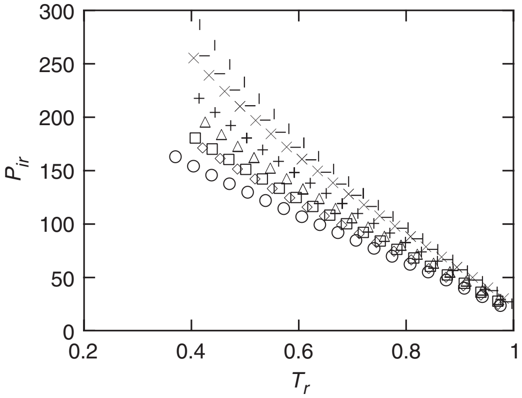

Figure 6. As in figure 2 for reduced internal pressure P_{ir}.

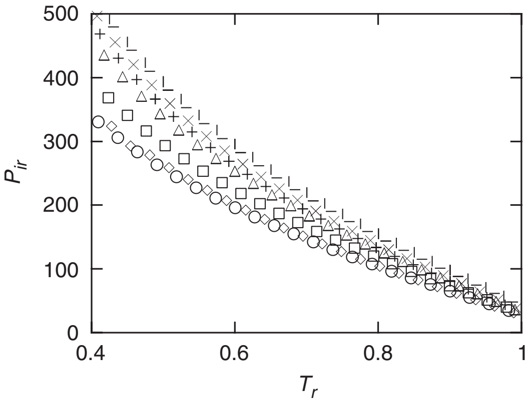

Figure 7. As in figure 3 for reduced internal pressure P_{ir}.

For each individual alkane a quadratic fit:

$$P_{ir} = a + bT_r + cT_r^2 \tag{20}$$

gives excellent results.

Again n appears as the better parameter for correlating the obtained coefficients. The results are:

$$a = 15.814 + 10.048n + 1.6495n^2 \tag{21}$$

$$b = 101.07 - 5.2118n - 3.449n^2 \tag{22}$$

$$c = -108.23 - 4.3585n + 1.8599n^2 \tag{23}$$

The percentage relative deviation is defined by (19) substituting Grüneisen's parameter for reduced internal pressure. Again we consider only the limit $T_r < 0.95$. The results thus obtained are shown also in figure 4. Although all alkanes are included, the methane presents an exceptional deviation ($\approx$10%). This case is very illustrative, revealing a very different behaviour with respect to the remainder and justifying its greater similarity with the simple liquids. Mean deviation is practically less than 5% for other cases. Its value is 2.8% for all alkanes jointly.

Also, the static structure factor at high wavelength $S(0)$ has been evaluated for all n-alkanes.

Figures 8–10 show the results for our three groups. For a more appropriate outlook, we plot $\ln S(0)$, instead of $S(0)$, against the reduced temperature. If T increases, the packing density η decreases and consequently $S(0)$ increases. Such behaviour is perfectly compatible with (15) and (16). A reasonable common behaviour that allows the application of the CSP can be observed. However, the fit is more difficult than in the remaining ones. In effect, whereas the ratio between the maximum and minimum values for Grüneisen's parameter and reduced internal pressure is 16 and 6 respectively, here this amount rises up 323.

Our proposed relation is:

$$S(0) = a + \frac{T_r^b e^{-cT_r}}{d - T_r} \tag{24}$$

with

$$a = 0.0057608 \tag{25}$$

$$b = 4.63 + 0.004852n + 0.014534n^2 - 0.00093258n^3 + 1.6795 \times 10^{-5}n^4 \tag{26}$$

$$c = 2.9113 + 0.036226n \tag{27}$$

$$d = 1.0046 \tag{28}$$

The percentage relative deviation is defined from (19) for this case and the limit for T_r is the same. Figure 4 shows a mean deviation greater than 10% only at the ends of the range. For the higher alkanes, the scarcity of experimental data explains this fact adequately. The global mean deviation is 6.5%.

In short, our analysis reveals that several quantities (Grüneisen's parameter, reduced internal pressure and static structure factor at high wavelength) show a similar

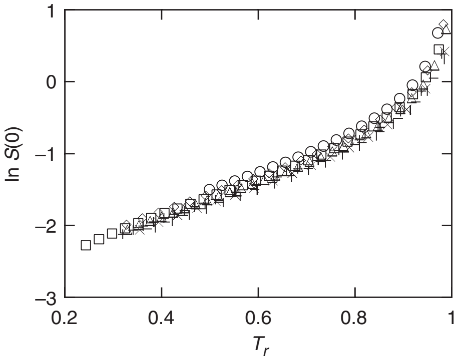

Figure 8. As in figure 1 for static structure factor at high wavelength *S*(0) (logarithmic scale).

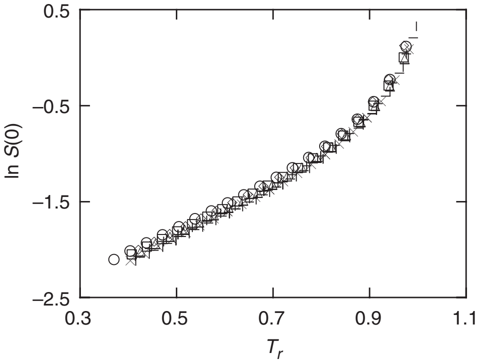

Figure 9. As in figure 2 for static structure factor at high wavelength *S*(0) (logarithmic scale).

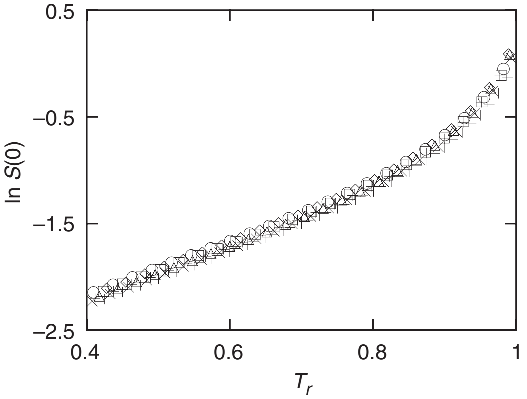

Figure 10. As in figure 3 for static structure factor at high wavelength *S*(0) (logarithmic scale).

behaviour for all analysed substances, along the liquid–vapour coexistence line for all alkanes when they are expressed in terms of reduced variables if a third parameter (atoms number of the molecule) is introduced. This behaviour guarantees the fulfilment of the CSP.

Our analytical expressions are highly estimable because our study includes a great number of substances and practically all liquid–vapour coexistence line. Particularly, methane and ethane differ appreciably with respect to the other alkanes for the three properties involved. For intermediate alkanes (n between 5–16) the mean deviation is less than 5% for the three properties except some isolated case. Extending its value to 10%, the same conclusion is valid for $n > 2$.

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