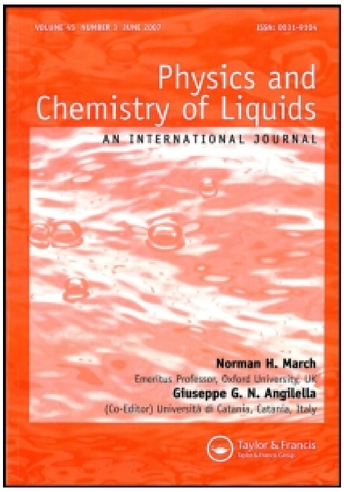

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Jan Thoen[a]
[a] Laboratorium voor Molekuulfysika, Departement Natuurkunde, Katholieke Universiteit van Leuven, Celestijnenlaan, Leuven, Belgium

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Asymmetry in the Homogeneous Phase Specific Heats at Constant Volume on the Coexistence Curve Near the Critical Point of Simple Fluids

JAN THOEN

Laboratorium voor Molekuulfysika, Departement Natuurkunde, Katholieke Universiteit van Leuven, Celestijnenlaan, 200D B-3030 Leuven, Belgium.

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It has recently been shown by Stephenson on rather general grounds that near the gas-liquid critical point of a simple fluid the specific heat at constant volume for the homogeneous vapor phase should become larger than the corresponding liquid value. In this paper experimental evidence, based on sound velocity data, in support of this result is presented. The experimental results also indicate strongly the equality of the leading singularities of C_v in the homogeneous liquid and vapor phases.

I INTRODUCTION

In a recent paper Stephenson[1] investigated the relation between the curvature of the vapor pressure curve of a pure fluid and the asymmetries between the coexisting liquid and gaseous phases. The curvature $(d^2p/dT^2)_\sigma$ could be related to the homogeneous phase specific heats at constant volume and the jump discontinuities in these quantities on entering the two phase region. It was also shown that in order to have a positive value for the curvature, as observed experimentally, one expects close to the critical point C_v to be larger for the saturated vapor than for the saturated liquid. Direct experimental specific heat data on the coexistence curve are scarce and inconclusive. In this paper I present indirect evidence for $C_{vg} > C_{vl}$ based on experimental sound velocity data in both coexisting phases. Attention is also paid to the amplitudes of the leading singularities of C_v in both phases.

II THEORETICAL RESULT

In this Section I summarize briefly the arguments of Stephenson[1] to arrive at the conclusion that $C_{vg}^{(1)} > C_{vl}^{(1)}$ for the homogeneous phases near T_c. The starting Eq. (1), derived by Yang and Yang,[2] relates the curvature of the vapor pressure curve $(\mathrm{d}^2p/\mathrm{d}T^2)_\sigma$ to the specific heat $C_v^{(2)}$ in the two phase region and the second temperature derivative of the chemical potential along that line.

$$\left(\frac{\mathrm{d}^2p}{\mathrm{d}T^2}\right)_\sigma = \frac{\rho C_v^{(2)}}{T} + \rho\left(\frac{\mathrm{d}^2\mu}{\mathrm{d}T^2}\right)_\sigma \tag{1}$$

From a combination of this equation for the liquid and the vapor side of the coexistence curve at the same temperature it follows that

$$T\left(\frac{\mathrm{d}^2p}{\mathrm{d}T^2}\right)_\sigma = \frac{C_{vg}^{(2)} - C_{vl}^{(2)}}{V_g - V_l} = \frac{(C_{vg}^{(1)} - C_{vl}^{(1)}) + (\Delta_g - \Delta_l)}{V_g - V_l} \tag{2}$$

In Eq. (2) Δ represents the jump in C_v in going from the one phase region to the two phase region and is given by:[3]

$$\Delta \equiv C_v^{(2)} - C_v^{(1)} = -T\left(\frac{\partial p}{\partial V}\right)_T\left(\frac{\mathrm{d}V}{\mathrm{d}T}\right)_\sigma^2 \tag{3}$$

Stephenson introduced the following explicit asymmetries in the quantities entering Eq. (2) and (3).

$$\left(\frac{\mathrm{d}\rho}{\mathrm{d}T}\right)_l = -\left(\frac{\mathrm{d}\rho}{\mathrm{d}T}\right)_g\left[1 + \mathrm{d}_1\frac{\rho_l - \rho_g}{\rho_c} + \cdots\right] \tag{4}$$

$$\left(\frac{\mathrm{d}p}{\mathrm{d}\rho}\right)_{Tl} = \left(\frac{\partial p}{\partial \rho}\right)_{Tg}\left[1 + \mathrm{d}_2\frac{\rho_l - \rho_g}{\rho_c} + \cdots\right] \tag{5}$$

$$C_{vl}^{(1)} = C_{vg}^{(1)}\left[1 + \mathrm{d}_3\frac{\rho_l - \rho_g}{\rho_c} + \cdots\right] \tag{6}$$

Asymmetries in $(\partial p/\partial T)_v$ can be related[1] to those in $(\partial p/\partial \rho)_T$ and $(\mathrm{d}\rho/\mathrm{d}T)_\sigma$. Inserting the asymmetries in Eq. (2) gives the following result:

$$\left(\frac{\mathrm{d}^2p}{\mathrm{d}T^2}\right)_\sigma \simeq -\frac{\mathrm{d}_3\rho_c C_{vg}^{(1)}}{T} + \frac{1}{\rho_c}\left(\frac{\partial p}{\partial \rho}\right)_{Tg}\left(\frac{\mathrm{d}\rho_g}{\mathrm{d}T}\right)^2[2 - 2\mathrm{d}_1 - \mathrm{d}_2] \tag{7}$$

By inserting in Eq. (7) power laws for the specific heat, the compressibility and the coexistence curve it can easily be seen that the first term on the RHS is the dominant one close to T_c if $\alpha > 2 - 2\beta - \gamma$. On the other hand it is known (from experiment) that the vapor pressure curve of simple fluids bends upwards and thus $(\mathrm{d}^2p/\mathrm{d}T^2)_\sigma > 0$. As a consequence d_3 should be negative and from Eq. (6) it follows that $C_{vg}^{(1)} > C_{vl}^{(1)}$.

From Rusbrooke's[4] exponent relation an alternative possibility for the exponents is $\alpha = 2 - 2\beta - \gamma$. In that case both RHS terms of Eq. (7) must also combine to give a positive result. Stephenson[1] has shown that this is achieved in $\mu - T$ scaling theory. In that case one has $\mathrm{d}_1 = 0$, $\mathrm{d}_2 = 1$ and $\mathrm{d}_3 < 0$.

Thus on quite general terms one obtains the somewhat surprising result that near T_c the specific heat at constant volume in the saturated vapor is larger than in the saturated liquid. It should however be noted that, if θ is the critical exponent for the curvature of the vapor pressure curve and α the exponent for C_v, the forms introduced for the asymmetries have as a consequence $\theta = \alpha$.

III EXPERIMENTAL VERIFICATION

Direct measurements of the specific heat C_v for the homogeneous liquid or vapor along the coexistence curve as a function of temperature are not realizable. As soon as the temperature is changed (to measure C_v) one leaves the coexistence curve along an isochore (for a temperature increase) or enters the two phase region (for a temperature decrease). Experimental C_v values for the homogeneous phases can be obtained as endpoints of measurements along isochores. To establish the T-dependence of $C_{vg}^{(1)}$ and $C_{vl}^{(1)}$ several isochores at liquid and gas densities have to be measured. There is no system where this very elaborate procedure has been carried out in sufficient detail close to the critical point to verify the conclusions given in Section II. For He^4 Moldover[5] reported measurements along seven near critical isochores. On the basis of these data no definite conclusion about the $C_{vg}^{(1)}/C_{vl}^{(1)}$ ratio can be obtained.

One can however try to derive values for C_v on the coexistence curve from an equation of state or from a thermodynamic quantity, which can be measured simultaneously in both coexisting phases. Such a quantity is the sound velocity. It can be measured simultaneously in the liquid and the vapor by placing an acoustic resonator in each of the coexisting phases.[6] One can also use a single variable-path-length interferometer and obtain the velocity from a measurement of the acoustic wavelength in each phase.[7,8] For the homogeneous phases the following relation between the sound velocity W and other thermodynamic quantities is valid.

$$W^2 = \frac{1}{\rho\kappa_T} + \frac{T(\partial p/\partial T)_v^2}{\rho^2 C_v} = \left(\frac{\partial p}{\partial \rho}\right)_T + \frac{T(\partial p/\partial T)_v^2}{\rho^2 C_v}. \tag{8}$$

In the RHS of Eq. (8) there are two diverging quantities: the isothermal compressibility κ_T and the specific heat C_v. Because the singularity in κ_T is much stronger than in C_v it turns out[6] that near T_c the behaviour of W^2 is almost completely determined by the last term. At a reduced temperature $T/T_c = 0.99$ for argon e.g. the contribution of the first term of the RHS is less than 5 % of the total for both the liquid and the vapor phase.

From Eq. (8) it is however also clear that it is not sufficient to have sound velocity data alone. One also needs at a given T values for the density and the slope of the isochore of that density upon entering the coexistence curve. For temperatures further away from T_c one needs also a rough estimate for the derivative $(\partial p/\partial \rho)_T$. To obtain these derivatives one can use an equation of state or at least pVT-data suitable for graphical determination of these slopes. In principle one can calculate $C_{vg}^{(1)}$ and $C_{vl}^{(1)}$ from an equation of state alone. In that case however one has to calculate also second derivatives. This usually results in rather large uncertainties particularly close to the coexistence curve and the critical point. In using the sound velocity, which can be measured accurately, one needs only first derivatives.

In Figure 1 the ratio $C_{vg}^{(1)}/C_{vl}^{(1)}$ for argon, methane and xenon is presented as a function of the quantity $(\rho_l - \rho_g)/\rho_c$. The results indicate, in accordance with section II, that $C_{vg}^{(1)} > C_{vl}^{(1)}$. All data points are based on sound velocity results. For the solid symbols values for the first derivatives and the density in Eq. (8) are derived from an equation of state. On the other hand graphical

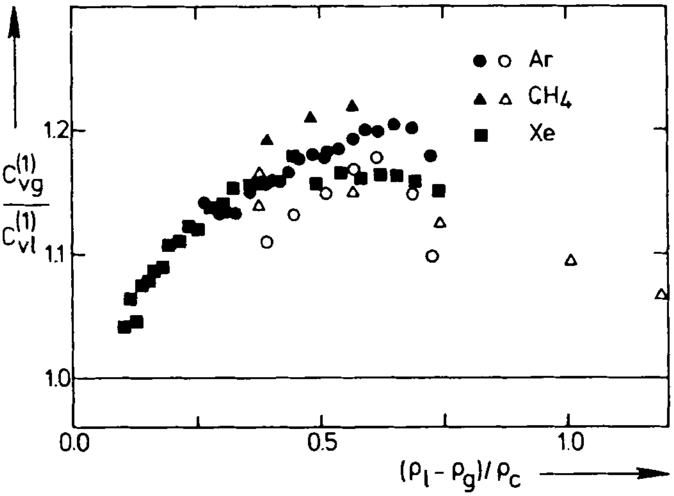

FIGURE 1 The ratio of the specific heat at constant volume in the homogeneous vapor and liquid phases along the coexistence curve as a function of reduced density difference near the critical point of argon, xenon and methane.

methods on direct experimental pVT-data were used in obtaining the derivatives to calculate ratio values represented by the open symbols. The empirical equation of state proposed by Verbeke *et al.*[9–11] was used. This equation of state developed for the critical region is consistent with the modern understanding of critical phenomena. It allows divergence of the curvature of the critical isochore and vapor pressure, and a singular diameter of the coexisting densities. These authors could successfully describe[11] their experimental pVT-data near the critical point of argon and methane. The equation was also used to fit[10] the pVT-data for xenon by Habgood and Schneider[12] and for He^4 by Roach.[13] It should be noted that data fitted with the equation covered a limited range around the critical point (±2K in temperature). Detailed results for the sound velocity in both coexisting phases are available for argon,[6] xenon[8] and methane.[14] In the investigation of methane by Gammon and Douslin[14] pVT-results were simultaneously obtained with the acoustic results. Since large acoustic dispersion is possible near the gas-liquid critical point [15,8] one has to make sure that low frequency thermodynamic values for the sound velocity are used in calculating the specific heat. Estimates on the basis of mode-mode coupling theory[15] showed that velocity dispersion was less than 1% for the data used to calculate the results for Ar and CH_4 given in Figure 1. For xenon low frequency (1.2 kHz) sound velocity data very close to the critical point are only available for the saturated vapor.[16] However results at ultrasonic frequencies (between 0.6 and 3 MHz) were obtained in both coexisting phases.[8] Close to the critical point there is a considerable amount of dispersion present in the ultrasonic data. On the basis of the low frequency data in the saturated vapor[16] and a mode-mode coupling analysis[8] it was possible to arrive at thermodynamic sound velocity values for the saturated liquid. The uncertainty on these values is estimated to be of the order of 1 to 2%. For the solid symbols for Ar, Xe and CH_4 I used the equation of state and the parameter values of Verbeke *et al.*[10,11] The sound velocity results for CH_4 came from a paper by Gammon and Douslin[14] and for Ar and Xe from Refs. 4, 8 and 16. To obtain the ratio values for Ar represented by the open circles I used the direct pVT-data of Ref. 11 and graphically determined the derivatives. The open triangles for methane are also based on graphically determined derivative values.[14] For this system ratio values over a larger $(\rho_l - \rho_g)/\rho_c$ range could be obtained. Further below T_c the ratio decreases and $C_{vl}^{(1)}$ becomes larger than $C_{vg}^{(1)}$ at a reduced density difference of 1.6 ($T/T_c = 0.90$).

The data points in Figure 1 clearly show that there is indeed close to T_c a range where $C_{vg}^{(1)} > C_{vl}^{(1)}$. Very close to T_c (a reduced density $(\rho_l - \rho_g)/\rho_c = 0.25$ corresponds to $T_c - T = 0.14$ K for xenon and $T_c - T = 0.08$ K for argon) the ratio values decrease and tend to a value of one at the critical point. This is expected if the amplitudes of the leading singularities in $C_{vg}^{(1)}$

and $C^{(1)}_{vl}$ are the same. The $(\rho_l - \rho_g)/\rho_c$ dependence of the ratio $C^{(1)}_{vg}/C^{(1)}_{vl}$ below $(\rho_l - \rho_g)/\rho_c < 0.5$ is also in qualitative agreement with a dominant linear contribution expected from Eq. (2) and expressed in Eq. (6).

The detailed behavior fo $C^{(1)}_{vg}/C^{(1)}_{vl}$ as a function of $(\rho_l - \rho_g)/\rho_c$ depends in a complicated way on the sound velocities, the densities and the slopes of isochores for both coexisting phases. However the limiting behavior of the ratio $C^{(1)}_{vg}/C^{(1)}_{vl}$ at the critical point, and thus the ratio of the leading singularities, is only determined by the sound velocity ratio. This can be seen by using Eq. (8) and writing the specific heat ratio as follows:

$$\frac{C^{(1)}_{vg}}{C^{(1)}_{vl}} = \frac{\rho_l^2\Gamma_{vg}^2 W_l^2[1 - \rho_l^{-1}\kappa_{Tl}^{-1}W_l^{-2}]}{\rho_g^2\Gamma_{vl}^2 W_g^2[1 - \rho_g^{-1}\kappa_{Tg}^{-1}W_g^{-2}]} \simeq \left[\frac{\rho_l^2\Gamma_{vg}^2}{\rho_g^2\Gamma_{vl}^2}\right]\frac{W_l^2}{W_g^2} \qquad (9)$$

with $\Gamma \equiv (\partial p/\partial T)_v$ the slope of an isochore. The terms involving the compressibility κ_T go to zero with an exponent $(\gamma - \alpha)$ and can be neglected for the range of interest here. The quantity between brackets in the last part of expression (9) has a value of one at the critical point, since there $\rho_l = \rho_g = \rho_c$ and $\Gamma_{vl} = \Gamma_{vg}$ if the inequality $\gamma + \beta > 1$ is satisfied,[1] which is the case experimentally. As a consequence any difference in amplitude for the leading singularity of C_{vg} and C_{vl} would also be present in the limiting behavior of the sound velocity ratio. From the direct experimental sound velocity data for argon, xenon and methane, it follows that the ratio W_l^2/W_g^2 reaches already a value of one at $t \equiv (T_c - T)/T_c$ of 10^{-3}. This corresponds to a value of 0.30 for the quantity $(\rho_l - \rho_g)/\rho_c$ of Figure 1. Within the experimental uncertainty this ratio remains one closer to T_c (data up to $t = 2 \times 10^{-5}$ for Xe and 2×10^{-4} for Ar). It should also be pointed out however that the ultrasonic data (at 0.6 to 3.0 MHz) for xenon show a small velocity inversion $(W_g > W_l)$ in the range $5 \times 10^{-5} < t < 5 \times 10^{-4}$. This effect is not larger than 1% and seems to disappear for points closer to T_c. Nevertheless the above experimental evidence strongly suggests that there is no leading order (α − divergent) asymmetry across the coexistence surface. As a consequence one would have[17] that the Griffiths[18] inequality $\theta < \alpha + \beta$ does not become an equality.

To estimate the uncertainty on the $C^{(1)}_{vg}/C^{(1)}_{vl}$ values would be very difficult. But from the fact that for the three systems investigated the ratio values agree rather well and do not depend very much on the method of calculation of the derivatives in Eq. (8) one can conclude that $C^{(1)}_{vg}$ is larger than $C^{(1)}_{vl}$ near T_c. In the immediate vicinity of the critical point the calculated ratio values are also consistent with a linear $(\rho_l - \rho_g)/\rho_c$ dependence. The values obtained for the $C^{(1)}_{vg}/C^{(1)}_{vl}$ ratio as well as the direct sound velocity data strongly suggest a limiting value of one at T_c. This leads to equal amplitudes for the leading singularities in $C^{(1)}_{vl}$ and $C^{(1)}_{vg}$.

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