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THERMOPHYSICAL PROPERTIES OF MATERIALS

The Speed of Sound and the Heat Capacity of Liquid Neon in the Subcritical Region[1]

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Abstract—The data (the speed of sound, the isobaric and isochoric heat capacities, as well as the heat capacity ratio) for liquid neon presented in the NIST Chemistry WebBook are analyzed. It has been shown, based on the representation of the inverse reduced volume fluctuations, that they consist of sufficient discrepancies in the subcritical region. The correction of data in this region of the coexistence curve is evaluated using the fluctuation approach and the theory of thermodynamic similarity.

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INTRODUCTION

Liquid neon finds applications in a wide range of cryogenic technologies since it has the advantage of a larger refrigerating capacity over other noble gases or liquid hydrogen [1, 2]. Additionally, one of the recent most promising applications is its usage in low energy particle detectors, in particular, for the observation of neutrinos [3] and for the search of the hypothetical particles of dark matter (WIMP). This is based on the fact of the better sensitivity of neon in comparison with liquid argon and xenon; a review of recent works can be found in [4, 5].

At the same time, the thermodynamic data for this liquid are not so extensively studied as those for other simple liquids, e.g., argon, which is in fact a standard for this kind of matter. This especially relates to the state parameters at high (for neon) temperatures, i.e., in the subcritical region (the critical temperature of neon is $T_c = 44.4$ K). A number of recently accepted practically applicable approximations of experimental data can be found in works [6, 7]. The fits proposed in the latter are also implemented in the modern standard reference online database NIST Chemistry WebBook [8].

A recent study of the volume fluctuations in liquid noble gases and the corresponding coexisting vapors under saturation conditions [9] has detected a certain irregularity in the plot of fluctuations in liquid neon in the subcritical region. Thus, the main goal of this work is to explore in detail the values of thermodynamic quantities (the speed of sound, the isobaric and isochoric heat capacities [8]) in the direct vicinity of the critical point and to discuss their more accurate approximations within this region.

[1] This article was translated by the authors.

METHODS AND RESULTS

The inverse ratio of the volume fluctuations in a condensed medium to its value for the hypothetical case of an ideal gas at the same thermodynamic conditions [9] reads as follows

$$\nu = \left[\frac{\langle(\Delta V)^2\rangle}{V}\Big/\frac{\langle(\Delta V)^2_{ig}\rangle}{V_{ig}}\right]^{-1} = \frac{\mu c^2}{\gamma RT}, \qquad (1)$$

where μ, c, γ, R, T are the molar mass, the speed of sound, the heat capacity ratio, the gas constant, and the temperature. Ratio (1) is a very sensitive parameter, which allows for exploring the microscopic structural characteristics of fluids based on macroscopically measurable quantities referring to the deviation of the latter from unity. It should be pointed out there is also a definite correlation of such an approach with the method of classic ideal curves on a thermodynamic surface [10] and correlations between the derivatives of thermodynamic functions in the subcritical region [11].

For simple liquids, the dependence of the parameter ν on the density along the coexistence curve varies from the exponential one in the region close to the melting point to the fractional power law under subcritical conditions. An example of the latter is presented in Fig. 1 for liquid argon as a function of the deviation of reduced density from unity

$$\log\nu_{\mathrm{Ar}} = 3.39\log(\rho_r - 1) + 0.911, \qquad (2)$$

where $\rho_r = \rho/\rho_c$, ρ_c is the critical density. The power index 3.39 agrees with the corresponding theoretical value [12] 3.673, which is known as slightly overestimating the real situation. The same behavior is noted for subcritical fluctuations in liquid krypton and xenon calculated using the data of [8].

It is important to note that the dependence in double-logarithmic coordinates for neon deviates suffi-

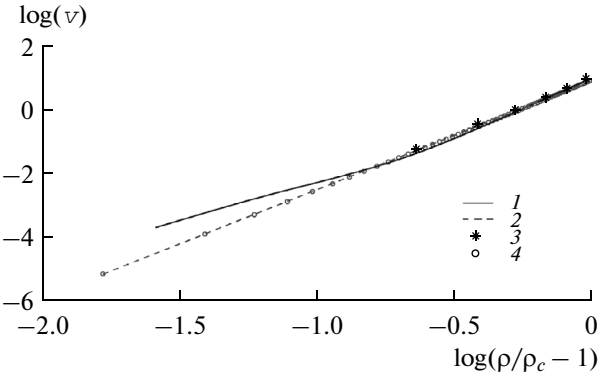

Fig. 1. The reduced volume fluctuations: *1* corresponds to the data of [8], *2* to [2] in liquid neon; *3* to [15], *4* to their approximation (8) in argon.

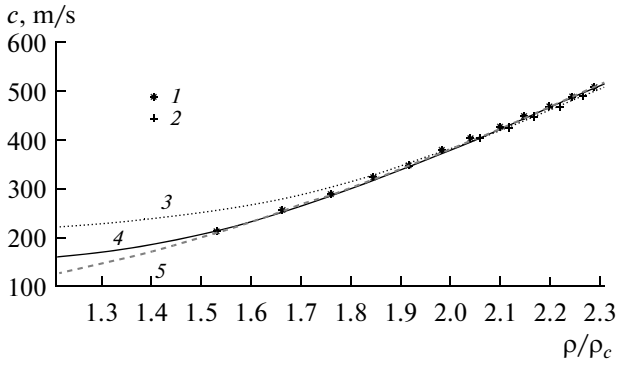

Fig. 2. The experimental data for neon: *1* corresponds to [15], *2* to [14], *4* to [8], *5* is the speed of sound in liquid argon along the coexistence line [8] rescaled as $c = 0.78c_{Ar}$.

ciently from linearity (see Fig. 1). However, there is no liquid–liquid structural transition located in this region that could demonstrate such behavior [13]. Thus, we need to explore the dependences of the speed of sound and heat capacities on the density, which are used in (1), to reveal the source of the error.

Figure 2 shows various available experimental values of the speed of sound in liquid neon along the coexistence line and the known approximation proposed in [14]:

$$c = A_0 + A_1T + A_2T^2, \qquad (3)$$

where $A_0 = 786.65$ m s^{-1}, $A_1 = 1.9754$ m s^{-1} K^{-1}, $A_2 = 0.33342$ m s^{-1} K^{-2}. It satisfies the data from [6] as well.

One can see that all the data agree well up to 37 K ($\rho_r = 2.06$), the last point of direct measurements evaluated in work [14] (Fig. 2, *2*). In addition, the quadratic fit (3) proposed there coincides with the experimental-based data [15] and both continual approximations [6, 8] up to 39 K ($\rho_r = 1.92$).

However, the divergence between the fits [6, 14] and the results [8, 15] grows within the interval $43 > T > 39$ K ($1.52 < \rho_r < 1.92$). This can be explained by the fact that the parabolic function of temperature is best adjusted to the reproduction of the speed of sound within the temperature interval $37 < T < 25$ K, where the actual measurements have been made. Its extrapolation to the practically subcritical region (as is done in [6]) does not have a foundation.

On the other hand, the NIST computational output is based on the experimentally verified values [15] for the region $43 > T > 39$ K ($1.52 < \rho_r < 1.92$) and, therefore, should be considered as confirmed within the mentioned interval. The table represents the relative errors for neon [8] and argon (rescaled data [8]).

The concluding region of discussion is the last 1.5 K before the critical point. As far as we know, there are no data of direct measurements within this interval. Therefore, the quality of the approximation proposed in [8] can be estimated only indirectly. Note that the speed of sound, the plot of which is shown as a solid line in Fig. 2, decays with decaying reduced density ρ/ρ_c much more slower for $T > 43$ K than for $T < 43$ K. The dotted line *3* representing the fit based on the smaller temperatures exhibits the same qualitative behavior. To check the supposition that the approximation [8], which provides a retarded decay of the speed of sound in neon, is the error source, we consider the behavior of values of the speed of sound in argon [8], which are confirmed by a larger amount of experimental data and are more warranted.

Such an approach is based on the facts of critical universality [12], which demonstrate a coincidence of thermodynamic parameters for substances having similar structure and the character of intermolecular interactions up to dimensionless scaling factors, and the theory of thermodynamic similarity [16] based on these facts. As a confirmation, one can see that the rescaled speed of sound in saturated liquid argon (line *3* in Fig. 2) fits the known experimental data for neon with a high accuracy. In addition, the approximation (3) for the speed of sound is even better within the interval $43 > T > 39$ K ($1.52 < \rho_r < 1.92$) than the fit *2* (Fig. 2) due to the smaller curvature in comparison with the latter (see table). Hence, the faster decay of the speed of sound in neon given by the rescaling of the values of argon for $T_c > T > 39$ K ($1 < \rho_r < 1.92$) could be argued as more physically realistic than those proposed by NIST.

Relative errors of approximation (%) of the isobaric and isochoric heat capacities and the speed of sound with respect to the data [15]

T, K	ε_{Cp} [8]	ε_{Cp}	ε_{Cv} [8]	ε_{Cv}	ε_c [8]	ε_c
40	0.8	−1.7	0.0	−0.7	−0.9	0.5
41	−0.6	−1.9	0.4	−0.1	−1.6	0.3
42	−8.5	−3.8	0.9	0.4	−0.5	0.2
43	−10.5	0.1	2.5	−0.3	−1.1	0.8

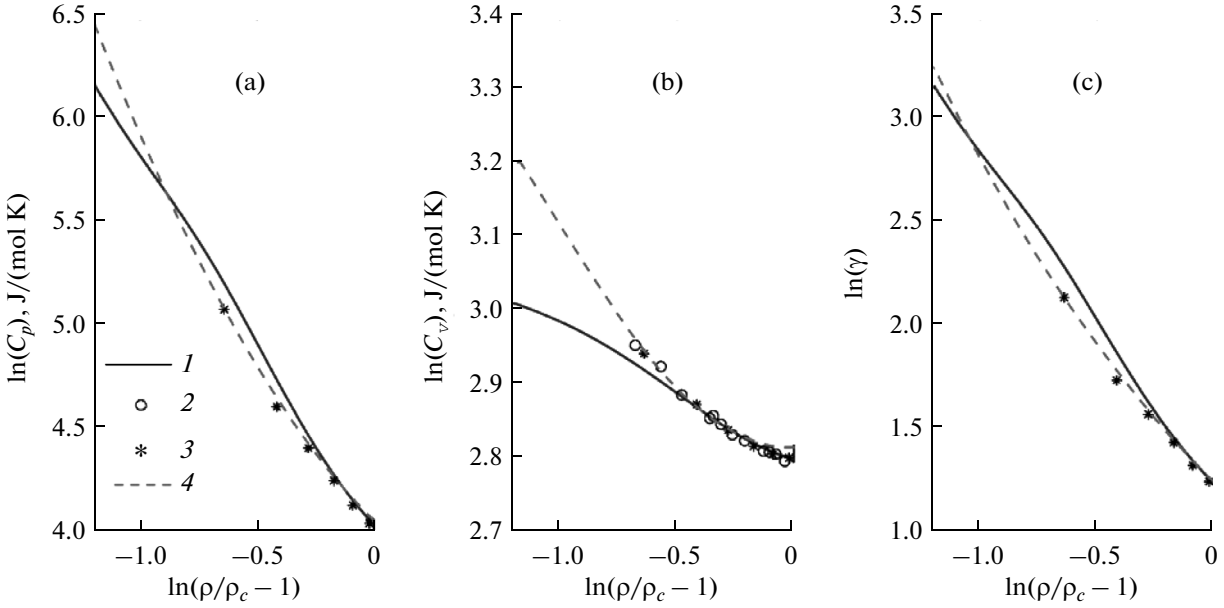

Fig. 3. The isobaric (a) and isochoric (b) heat capacities and their ratio (c): *1* corresponds to the data of [8]; *2* to the direct measured data [15]; *3* to the processed data [15]; *4* to the data for argon [8] multiplied by 0.93.

Now let us consider the isobaric and isochoric heat capacities, the ratio of which is also used in (1). The corresponding plots are presented in Fig. 3. One can see that all data provided by NIST in the temperature interval from 40 K ($\rho_r - 1$) up to the critical point demonstrate significant discrepancies. This conclusion follows, first, from their deviation from the experimental data [15] and, second, from the shapes of curves represented in the logarithmic scale. As for the latter, the general theory of critical phenomena [12] claims a strict power-law divergence of the heat capacities approaching the critical point. Therefore, the plots should be straight lines in logarithmic coordinates. But the solid lines do not satisfy this condition (Fig. 3): the isobaric heat capacity curve weakly oscillates around the straight line, and the isobaric heat capacity not only deviates from the basic experimental data but even slows its growth approaching the critical region. The table shows the continuous growth of the relative errors for both heat capacities as the temperature approaches the critical one. As a result, the plot of the ratios of the heat capacities in Fig. 3 has a "hump," which corresponds to deviating line in the plot representing the reduced fluctuations (Fig. 1).

On the other hand, it is possible to repeat the rescaling procedure for NIST's data on argon with the goal to obtain a better approximation for both heat capacities of neon. The corresponding dependencies $C_{p,V} = 0.93C_{p,V(\mathrm{Ar})}$ are shown in Fig. 3 as dashed lines. They coincide quite well with the real experimental data [15] within the interval $43 > T > 39$ K and keep the linear character in logarithmic coordinates, i.e., a power-law divergence, when tending to the critical point.

CONCLUSIONS

The present study shows that the calculated approximation, which is realized in the database NIST Chemistry WebBook [8] based on the algorithm from [7] can be considered as reliably for the acoustic and thermophysical data for liquid neon along the coexistence curve up to 40 K only. However, the results [8] deviate sufficiently from the actual experimental and physically expected (in particular, from the point of view of a general theory of general critical phenomena) data within the subcritical region 40–44.49 K. Therefore, the fit adjusted to the states far from the critical point cannot be extrapolated to its vicinity. In addition, this region covers a temperature interval of about a few Kelvins. Hence, small deviations of the temperature used as an independent variable during its fitting may result in large deviations of other state parameters.

On the other hand, the density varies sufficiently over this small interval of the temperature variations. An additional amplification of the sensitivity is provided by the application of the reduced volume fluctuation approach [9].

Thus, the processing of thermodynamic parameters from the NIST database included into (1) shows that they all require corrections for $T > 10$ K. But this correction can easily be evaluated by the corresponding rescaling (the coefficients are given in the work) of the NIST data for liquid argon.

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