The equation of state and the isochoric specific heat near the critical points of liquids

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The specific heat of ethane was measured in the gravitational field and the results are compared with the specific heat of the homogeneous system. It turns out that in the temperature region above the critical temperature the presence of the gravitational field leads to a decrease in the specific heat, whereas the opposite result follows from the analysis of all the existing equations of state near the critical point. In this connection, the existing calorimetric experiments near the critical points of other substances are critically analyzed.

1. FORMULATION OF THE PROBLEM

The efforts of many investigators are at present directed at finding the critical indices characterizing the singularities of the thermodynamic quantities as we approach the critical point along different paths in the phase diagram. The equation of state is determined, as a rule, by interpolation, i.e., by constructing the function from the known set of its limiting values.

According to the so-called "linear model," the equation of state is determined by eliminating the variables r and θ from the following system of equations[1]:

$$\begin{gathered}\mu(\Delta\rho, t) - \mu(0, t) = ar^{\beta\delta}\theta(1-\theta^2);\\ t = r(1-b^2\theta^2), \quad b^2 = (\gamma-2\beta)/\gamma(1-2\beta),\\ \Delta\rho = kr^\beta\theta.\end{gathered} \tag{1}$$

The second and third equations in (1) determine the transition in the $\Delta\rho - t(\Delta\rho = (\rho - \rho_c)/\rho_c$, $t = (T - T_c)/T_c)$ plane to curvilinear polar coordinates, all the singularities being contained in the dependence of the equation of state on r. The choice made for the angular functions in the Eqs. (1) is the simplest that determines the isochor ($\theta = 0$), the critical isotherm ($\theta = \pm 1/b$), and the coexistence curve ($\theta = \pm 1$).

A. A. Migdal[2] has derived the equation of state on the basis of the assumption that the equation of the isocline is analytic[2]:

$$\zeta\chi^{(\beta+\gamma)/\gamma} = \varphi(\Psi\chi^{\beta/\gamma}); \tag{2}$$

here Ψ and ζ are the order parameter and the field conjugate to it, while χ is the generalized susceptibility. The only result obtained from general considerations is the oddness of the function $\varphi(m)$ in (2). Allowance for the terms of order m and m^3 leads to the equation of state (1) with the additional requirement that $\beta + \gamma = 3/2$, while the addition of terms of order m^5 leads to the presence of corrections in $\beta + \gamma - 3/2$ $^{1)}$. However, these corrections do not, in the case of interest to us, lead to a qualitative change in the results, and therefore we shall henceforth consider the equation of state of the "linear model."

Another form of the equation of state proposed by Vicentini-Missoni, Levelt-Sengers, and Green[3] is connected with a purely empirical choice of the form of the function h(x), where $x = t/|\Delta\rho|^{1/\beta}$:

$$h(x) = E_1\left(\frac{x+x_0}{x_0}\right)\left[1+E_2\left(\frac{x+x_0}{x_0}\right)^{2\beta}\right]^{(\gamma-1)/2\beta} \tag{3}$$

in the scaling-law equation of state

$$\mu(\Delta\rho, t) - \mu(0, t) = \operatorname{sign}(\Delta\rho)\,|\Delta\rho|^\delta h(x). \tag{4}$$

The equations of state (1)—(4) have been quite thoroughly compared with the experimental data—mainly with P-ρ-T measurements[1,3,4]. On the whole the results turned out to be satisfactory: two constants (a and k) in the case (1) and three (E_1, E_2, x_0) in cases (3) and (4), in addition to the critical indices, turned out to be sufficient for a reasonable quantitative agreement of Eqs. (1), (3), and (4) with experiment, and the values of the constants for substances of the same kind are extremely close.

We wish to draw attention to the behavior of a pure liquid near the liquid-vapor critical point in the presence of gravity, i.e., of a system which is inhomogeneous in density, and in the "ideal" case when the system is homogeneous, the question to be discussed being the isochoric specific heat C_V. The "ideality" of the system can apparently be achieved by decreasing the height of the vessel with the liquid[5], or by introducing a stirring system[6] (although the latter has to be specially investigated in each specific case[7,8]). It turns out that there exists a qualitative discrepancy between the results of experiments with different substances, a discrepancy which cannot be eliminated by selection of constants in the equation of state. It is possible that it is precisely such experiments that will turn out to be decisive in judging the validity of the existing equations of state of a liquid in the critical region.

In the presence of gravity the liquid becomes substantially inhomogeneous (the density differentials attain 10% for a vessel of height $H_m \sim 1$ cm), which leads to a change in the temperature dependence of C_V. The corresponding simple computation was first carried out analytically by us[9], using a simplified equation of state[10]. A similar computer calculation of $\overline{C}_V(T)$ has been carried out for equations of the form (1)[11] and (3), (4)[12]. It turns out that the specific-heat maximum shifts towards the two-phase region and is found at $t \sim (\rho_c g H_m/P_c)^{1/\beta\delta}$, while the value of the C_V at the critical point $T = T_c$ is, of course, proportional to $(\rho_c g H_m/P_c)^{-\alpha/\beta\delta}$.

In the region $T > T_c$, which we shall henceforth consider, two possibilities can, generally speaking, be realized—see the figure. Let the mean density in the vessel be equal to the critical density $\bar{\rho} = \rho_c$. Then the specific heat of the inhomogeneous system is obtained by averaging over the height of the vessel the quantity (for greater details, see[9])

$$C_H \approx C_V(T,\rho) + \left(\frac{\partial S(T,\rho)}{\partial\rho}\right)_T\left(\frac{\partial\rho(T,H)}{\partial T}\right)_H. \tag{5}$$

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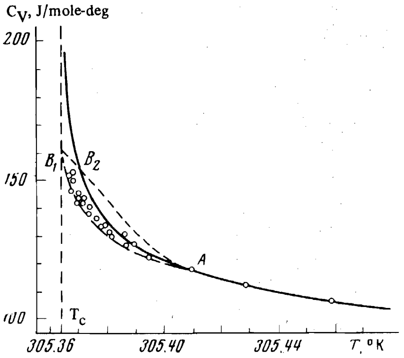

FIG. 1. The specific heat of a liquid near the critical point. The continuous curve corresponds to the experimental values of the "ideal" specific heat of ethane described by the equation $C_V/T = (0.125t^{-0.13} - 0.005)$ J/mole-deg^2 [7,8] and the points represent the specific heat of ethane in the gravitational field.

The averaging of the first term in (5) leads to a decrease in the value of the specific heat as compared to the "ideal" system, when $\rho = \rho_c$ in the whole liquid, and it is, in particular, the cause of the finiteness of the specific heat at $T = T_c$. But as we move away from $T = T_c$, the inhomogeneity in the density decreases, i.e., the averaging of the second term in (5), a term which is not at all present in the "ideal" case, makes a positive contribution to the measurable specific heat. Therefore, for the temperature region under consideration, we cannot, generally speaking, say beforehand which system—homogeneous of inhomogeneous—will have a higher specific heat. In accordance with which of these effects predominates, a dependence of the type of the curve B_1A, or of the curve B_2A in the figure is possible2).

In the case of the B_2A curve, it is also important where the point B_2, which is the point of intersection of the "ideal" and the gravity-influenced specific-heat curves, is located. If B_2 is located near the point A, where both curves practically coincide, then the difference between the curves B_1A and B_2A is not too important. If, however, B_2 is located near $T = T_c$, as shown in the figure, then the specific heat C_V of the "ideal" system is smaller than the specific heat C_V in the gravitational field in a wide range of temperatures.

The existing experimental data do not allow us to uniquely solve the problem of the behavior of the C_V in the gravitational field, since for argon[6] and helium[14] the case B_1A is realized, while for CO_2[5] and xenon[15] the case B_2A is realized. It might be thought that an equation of state of the type (1) or (3), (4), for example, leads, depending on the parameters of the substance, to both curves B_1A and B_2A, or (in the case B_2A) to a situation where the location of the point B_2 varies from substance to substance. No contradictions would in this case arise between the above-indicated experiments.

In Sec. 2 we present the results of the measurements of the C_V of ethane in the gravitational field and give account of the special measures we employed to ensure the reliability of the experimental data. The importance of these measures for the analysis of experiments with other substances[5,6,13,15] and the results following from (1) and from (3) and (4) form the content of Sec. 3.

2. EXPERIMENT

The difficulties encountered in calorimetric experiments in the critical region have been repeatedly discussed[7,16,17]. In the case discussed here these difficulties were especially great, since it was desirable to investigate in one experiment a system located in a gravitational field and substantially inhomogeneous in density, as well as an "ideal"—homogeneous in density—system. Both experiments—with stirring of the substance and without stirring—were carried out in one and the same calorimeter of height 2.5 cm. The adiabatic-calorimeter technique was chosen[18]. Such type of setup has been described in detail, and therefore we shall dwell only on the improvements introduced to allow us make the results of the experiment more reliable.

A capillary was usually used to fill the calorimeter with the substance, and the locking valve was located outside the vacuum sleeve. Such a construction is convenient in many respects, but there arises in this case an uncertainty in the quantity and even about the thermodynamic state of the substance. Therefore a high-pressure split valve was constructed[19] and mounted directly on the calorimeter. The capillary was then entirely eliminated.

In order to decrease the influence of the temperature gradients on the results of the measurements, the calorimeter was surrounded with an isothermal sheath, a copper layer ~0.3 mm thick, galvanically deposited on the outer surface of the calorimeter, which was made of stainless steel. The largest possible temperature gradient observed at the surface of the copper coating under the most unfavorable conditions of the experiment did not exceed 10^{-4} deg/cm. The improvements which were introduced into the construction of the thermal shields and into the thermocontrol system led to the decrease of the temperature gradient in the shields to the same level[7,8].

The effect of the decrease in the temperature gradients on the thermal-equilibrium establishment times is interesting. In the previous experiments (see, for example,[6]) these times increased to 5—6 hours for $t \sim 10^{-4}$. In the experiments described here (in the region $T > T_c$) these times were only a few minutes and did not depend on stirring3).

To eliminate the inhomogeneity in the density along the height of the vessel, we used a stirrer of special construction[7,8]. The power evolved during stirring did not exceed 10^{-4} W, which is at the level of the power evolved by a platinum resistance thermometer. Various operating conditions of the stirrer and their effect on the results of the specific-heat measurements were specially investigated[7,8].

The interpretation of the results of the experiment in the critical region essentially depends on the correct choice of the critical temperature T_c, but the "smearing out" of the singularity in the gravitational field practically excludes the correct choice of T_c from such an experiment. We used three methods to determine T_c: the most accurate method was the method of quasi-static thermograms[7,20]; the others were the determination of T_c from measurements of C_V of the ideal system (with stirring) when the C_V singularity is sufficiently strongly pronounced, and, finally, the determination of T_c from the maximum of the equilibrium establishment times in the experiment without stirring. It was established by special experiments[8] that all these three methods give, to within 0.0005°, the same value 305.3633°K for the critical temperature of ethane (in the intrinsic scale of the thermometer).

The specific heat C_V of ethane measured in the gravitational field ($T > T_c$).

T_1, °K	T_2, °K	C_V, J/mole × deg	T_1, °K	T_2, °K	C_V, J/mole × deg
305.3641	305.3684	152.0	305.3737	305.3838	134.5
305.3647	305.3690	146.8	305.3741	305.3790	133.4*
305.3649	305.3700	150.0*	305.3757	305.3849	131.5
305.3652	305.3694	152.7	305.3774	305.3865	132.9
305.3666	305.3710	142.5	305.3814	305.3900	131.3*
305.3671	305.3715	145.8	305.3811	305.3904	127.5
305.3672	305.3715	143.5	305.3840	305.3934	127.5
305.3690	305.3734	142.5	305.3892	305.3987	122.3
305.3691	305.3735	143.8	305.3978	305.4186	118.7
305.3689	305.3778	138.6	305.4175	305.4387	112.5
305.3711	305.3755	140.8*	305.4374	305.4795	107.3
305.3709	305.3799	136.8	305.4784	305.5213	102.0

T_1 and T_2 are the temperatures at the beginning and end of the calorimetric experiment.

The results of the measurement of the specific heat of ethane with and without stirring are shown in Fig. 1 and in the table. It can be seen that the specific heat of the inhomogeneous system does not exceed the specific heat of the "ideal" system at all the investigated temperatures4). We proceed to compare this result with the conclusions of other authors and with the computations carried out with the existing equations of state.

3. DISCUSSION OF THE RESULTS

In view of the already mentioned qualitative discrepancy between the results of the various experiments on the measurement of specific heat in the gravitational field, it is necessary to analyze the most important factors that influence the results of the experiments. Such factors are, in our opinion, the existence of temperature gradients and the nonequilibrium connected with these gradients, as well as the choice of the critical temperature.

In a system near the critical point, the temperature gradients take the longest time to even out[21]. Therefore, the decrease of these gradients is the principal problem to be solved in order to obtain reliable specific-heat values that correspond to a system in thermodynamic equilibrium. An interesting example—pertaining, to be sure, to mixtures and not to pure substances—of the effect of temperature gradients on the properties of a liquid near the critical point is the inhomogeneity in the concentration along the height detected by Blagoĭ and his collaborators[22] near the critical lamination point of a $CH_4 - CF_4$ mixture. Subsequent experiments performed by these same authors showed that the inhomogeneity was a result of the existence in the system of small (of the order of 0.002 deg/cm) temperature gradients[23]. The special measures that were taken to eliminate the temperature inhomogeneity led to the disappearance of the inhomogeneity in the concentration.

Besides the temperature gradients, of decisive importance for the interpretation of the results of the specific-heat measurement in the gravitational field is the correct choice of T_c. This circumstance is conveniently illustrated by the Edwards-Lipa-Buckingham experiment on xenon[15], in which temperature gradients were practically eliminated and the measurements were, to a sufficient degree, equilibrium measurements—in any event, in the homogeneous-state region. However, these authors did not simultaneously carry out the "ideal" experiment in which T_c would have been determined, and therefore they had to find T_c by fitting. It turned out in this case that T_c was located near the gravity-influenced specific-heat maximum, which, as has already been noted, is shifted by the amount $t \sim (\rho_c g H_m / P_c)^{1/\beta\delta}$ towards the temperature region below the critical temperature—see Fig. 2 in[15]. The same figure (i.e., Fig. 2 in[15]) shows the equilibrium-establishment time curve for the system, a curve whose strongly pronounced peak does not, it turns out, coincide with the critical temperature chosen by the authors. The existence of another distinct temperature is physically totally unjustified and, in our opinion (for details, see[24]), we must choose as T_c just the temperature of the maximum of the equalization times (i.e., the data of the experiment[15] should be processed with a higher value for the critical temperature).

It turns out that if we so choose T_c, then the results of the Edwards-Lipa-Buckingham experiments on xenon qualitatively change: the $\overline{C}_V$ in the gravitational field is located below and not above the specific-heat curve of the ideal system, i.e., the case B_1A and not B_2A in the figure is realized. If the data obtained by us on ethane are processed not relative to a correctly chosen T_c, but relative to the maximum of $\overline{C}_V$ in the gravitational field, then the $C_V(T)$ curve for ethane will also have the form of the curve B_2A instead of the correct B_1A. Thus, the correctly processed experiments on xenon[15] agree with our experiments on ethane: the $\overline{C}_V$ in the gravitational field is less than the "ideal" specific heat at all temperatures near the critical point5).

The design of the calorimeter used by Edwards, Lipa, and Buckingham to measure the specific heat of CO_2[5] was extremely ingenious. The calorimeter was a low, thin-walled, stainless-steel cylinder whose height was roughly 15 times smaller than the diameter. The "ideal" specific heat is measured (without stirring) with the calorimeter in its normal position, while the specific heat in the gravitational field is measured with the calorimeter tilted. The results of the experiment with CO_2 turned out to be at variance with our results; there is a temperature region where the $\overline{C}_V$ in the gravitational field is larger than the "ideal" specific heat. Unfortunately, the material in[5] is expounded extremely briefly and methodological questions are not at all discussed; therefore, it is not possible to carry out a thorough analysis of the experiment described there. It is possible that temperature gradients appear in the substance when the calorimeter is in the vertical position. The low critical-temperature value used in[5] for CO_2 is extremely surprising: $T_c = 30.775°C$, whereas the generally accepted value[3] is $T_c = 30.94 \pm 0.01°C$. Before Edwards, Lipa, and Buckingham publish a detailed report about their work with CO_2, or before we perform the special experiment we have planned on this substance, it will be difficult to draw any conclusions about the comparison of the results of the indicated experiment with ours.

Let us now proceed to the theoretical analysis of the behavior of the $\overline{C}_V$ in the gravitational field. Our previous calculation[9] showed that as compared to the specific heat of the "ideal" system the $\overline{C}_V$ is depressed by the gravitational field at all temperatures. We, however, used a simplified equation of state that admitted of an analytical investigation[10], and these results cannot therefore be considered as final. Barmatz and Hohenberg[11] used the equation of state (1) and Schmidt[12] the equations (3) and (4) for a numerical computation of the $\overline{C}_V$ of xenon and obtained an appreciable overestimate for the specific heat in the gravitational field in a fairly wide range of temperatures. In the opinion of the indicated authors, these computations agree with the experiments on xenon[15]. As we have already said, we hold the opposite view on this score. Barmatz and Hohenberg explain, without any specific justification, the discrepancy between their computation and other experiments as due to a systematic error in the case of argon[6] and an incorrect choice of T_c for helium[14].

We have carried out a special analysis of the equations of state (1) and (3), (4) with a view to elucidating, without recourse to a numerical calculation, the conditions under which situations of the type described by the curve B_1A or B_2A can be realized.

First of all, using the expressions for the chemical potential (1), (3), and (4) and the equation of hydrostatics, we easily find the density distribution along the height for each temperature. The obtained expression, as well as the functions $C_V(T, \rho)$ and $(\partial S(T, \rho)/\partial\rho)_T$ determined on the basis of the equations of state, should be substituted into the formula (5) and the resulting expression averaged over the height of the calorimeter. We omit all the details of the computation and quote only the result. In the vicinity of the point A in the figure, i.e., in the temperature region $t \gg t_0 \sim (\rho_c g H_m/P_c)^{1/\beta\delta}$, for the equation of state (1) the measurable specific heat in the gravitational field is equal to ($h_m = \rho_c g H_m/P_c$)

$$\bar{C}_V = \frac{ak}{2\alpha b^2}\frac{\gamma(\gamma-1)}{t^\alpha}\left\{1+\frac{h_m{}^2 b^2}{12a^2 t^{2\beta\delta}}\left[-\alpha + \frac{2\gamma^2}{1-\alpha}\left(\frac{(\gamma-\alpha)(1-2\beta)}{\gamma(\gamma-1)}-1\right)\right]\right\}, \tag{6}$$

while for the equation of state (3), (4)

$$\bar{C}_V = \frac{C(2-\alpha)(1-\alpha)}{t^\alpha}\left\{1+\frac{\gamma(\gamma+1)}{24(2-\alpha)(1-\alpha)}\cdot\frac{x_0{}^\gamma}{CE_1E_2^{(\gamma-1)/2\beta}}\frac{h_m{}^2}{t^{2\beta\delta}}\right\}, \tag{7}$$

where $C = C(\alpha)$ (see[3]).

It can be seen from (5) and (6) that the sign of the correction to the "ideal" specific heat due to the gravitational field, which is determined by the terms standing next to the number one in the curly brackets, is wholly connected with the universal critical exponents and not with the parameters of the equation of state, which change from substance to substance, these corrections being positive for all reasonable values of the exponents[6]. Thus, all the equations of state near the critical point that are used at present lead to a situation of the type B_2A in the figure and not to B_1A.

We still have to consider the question of the dependence of the position of the point of intersection B_2 of the specific-heat curves on the parameters of the equation of state. Had the point B_2 been, at least for some substances, located near the point A, the narrow temperature range corresponding to B_2A could have remained experimentally unnoticed. Using the equation of state (1), we obtain for the coordinate of the point B_2 the following expression:

$$t_{B_2} = \left[\frac{(\gamma-1)^2(3\beta+2\gamma-2)}{\beta(\gamma-1)^2+\gamma(1-2\beta)^2}\right]^{1/\alpha}\left[\frac{1}{b}\left(1-\frac{1}{b^2}\right)\right]^{-1/\beta\delta} \times\left(\frac{h_m}{2a}\right)^{1/\beta\delta}\left\{1+\frac{1}{2}\left[\frac{(\gamma-1)^2(3\beta+2\gamma-2)}{\beta(\gamma-1)^2+\gamma(1-2\beta)^2}\right]^{1/\alpha} \times\left(\frac{3\beta+2\gamma-2}{3\beta+2\gamma-3}\right)\left[\frac{\gamma(1-2\beta)-\beta(\gamma-1)}{\beta(\beta+\gamma)(\gamma-1)}+\frac{(\beta+\gamma)(\gamma-1)}{\gamma[\beta(\gamma-1)^2+\gamma(1-2\beta)^2]} \times\left(\frac{4\gamma(1-2\beta)(1-2\alpha)}{\alpha(1-\alpha)}-\frac{\gamma^2(\gamma-2\beta)^2}{(\beta+\gamma)^2(\gamma-1)^2}\right)\right]\right\} \sim 10^{-3}\left(\frac{h_m}{a}\right)^{1/\beta\delta}. \tag{8}$$

In view of the universality of the critical exponents, the quantity t_{B_2} can change from substance to substance owing to the variation of the parameter a, which changes by roughly a factor of three ($a \approx 25$ for xenon and CO_2, and ≈ 8 for helium). Thus, the position of the point B_2 depends weakly on the substance (a similar result is obtained for the equation of state (3), (4)), and the temperature range corresponding to B_2A is quite wide: for CO_2 it is equal to 0.07 deg[5].

Thus, the presently existing equations of state lead in a fairly wide interval near the critical point to an overestimate of the specific heat $\bar{C}_V$ in the gravitational field as compared to the "ideal" specific heat. Our experiments on ethane, as well as the experiments on xenon[15] and, apparently, on argon[6] and helium[13], lead to the contrary dependence (the experiment on CO_2[5] needs to be specially analyzed). It is possible that the measurements of the specific heat of the inhomogeneous (in the gravitational field) and the homogeneous liquid will turn out to be fundamentally important for the solution of the problem of the equation of state of a substance near the critical point.

[1] We constructed the equation of the isocline in the "linear model," and it turned out, in the approximations considered by Migdal, to differ from Migdal's equation by a small quantity in the parameter $\beta + \gamma - 3/2$.

[2] Of the same origin is the result, which, on the face of it, is paradoxical, that the singularity in the susceptibility is stronger in the inhomogeneous case than in the "ideal" case [13].

[3] To verify this, the duration of the experiment was extended to 15-20 hours at some temperatures; the result did not change (such points are marked with an asterisk in the table). We could not on our equipment reliably determine equilibrium establishment times of more 20 hours. Thus, we assume that in the experiments with stirring and without stirring of the substance the state of the system under measurement was an equilibrium state (if, of course, the equilibrium establishment times did not, as we approached the critical point, exceed 20 hours).

[4] In Fig. 1 we show the specific-heat curve for the "ideal" system. For $t < 10^{-4}$ the value of the specific heat of the "ideal" system depends on the stirring regime [7,8], but all the experimental points, irrespective of the stirring regime, lie above the corresponding values of the specific heat of the system without stirring.

[5] The results of the experiments on argon [6] and on helium [14] also agree with our conclusions, i.e., the inhomogeneity of a system in a gravitational field leads to a reduction in its specific heat as compared to the specific heat of the "ideal" system. We cannot, however, consider them to be sufficiently reliable: the results of [6] could have been distorted by temperature gradients, while the presence of the "cold" capillary in the experiment [14] introduces a significant uncertainty into the effective height of the calorimeter and its dosage. We do not carry out a more thorough analysis of the data on argon and helium, since we consider the data on Xe [15], CO_2 [5], and on ethane [7,8] to be more reliable.

[6] A qualitatively similar result is obtained for the equation of state (2).

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