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SPLITTING OF THE SPECIFIC-HEAT MAXIMUM AND DISCONTINUITY NEAR THE CRITICAL POINT

A. T. BERESTOV and S. P. MALYSHENKO

Institute of High Temperature Physics, U.S.S.R. Academy of Sciences

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Experiments show[1] that the specific heat C_V^{bs} of a binary system as a function of temperature does not lie on the coexistence curve near the critical point, i.e., it does not coincide with the specific heat discontinuity. This effect is not the result of impurities in the system but rather the result of an inhomogeneity of the matter along the height of the calorimeter, which persists even during stirring. The calculation results agree satisfactorily with the experiments, and the evaluated inhomogeneity parameter is reasonable (reasonable values are also obtained for the isothermal density-distribution relaxation time). The presence of impurities and small temperature gradients in the sample modify the specific-heat peak splitting and discontinuity and lead to additional distortion of the singularity. A similar behavior is also observed in solids near second-order phase transition points; this, apparently, can likewise be attributed to external actions on the system, e.g., nonuniformity of the ordering parameter in the sample, due for example to an external nonuniform field or to inhomogeneities that are produced during the preparation of the sample and are not in thermodynamic equilibrium with the lattice.

1. THE experimental data[1] show that the specific heat has a peculiar temperature dependence near the critical point of liquid and near the second-order phase transition point, namely, at a nonzero value of the ordering parameter, a maximum of the specific heat is observed; the position of this maximum does not coincide in temperature with the jump of the specific heat connected with the appearance of the second phase, with $T_{max} < T_j$. The magnitude and position of the maximum of the specific heat and the splitting of the maximum and of the jump depend on the average value of the ordering parameter (on the density of the medium in the calorimeter in the case of the critical point of a liquid).[1, 2] Thus, experiments indicate that there is one more distinct line on the P-V phase diagram, namely the line of maxima of the specific heat of the binary system, C_V^{bs}, located inside the coexistence curve. This line has a maximum at the critical density and is similar in shape to the coexistence curve (see Fig. 1 below). At the same time, the maximum specific-heat curve has nothing in common with the spinode, since the existence of metastable states of the liquid in the calorimeter was excluded in the experiments of Voronel' et al.[1]

It can be shown that the distortion of the character of the specific heat as a result of the presence of impurities in the system does not lead to the appearance of a dome-like line of maxima of C_V^{bs}. In the absence of an external field and other external actions on the system, the specific heat of a mixture with fixed composition x depends only on the average specific volume $\overline{V}$ and the temperature T. In the presence of two coexisting phases in the system, the intensive properties of each phase depend only on the temperature, and the amount of matter in the phases is determined by the average specific volume V, i.e., the specific heat of a binary mixture of fixed average composition $\overline{x}$ depends linearly on V. For example, in the case of a single-component system

$$C_V^{bs} = C_{V_2} - T\left(\frac{\partial P}{\partial V_2}\right)_T \left(\frac{\partial V_2}{dT}\right)^2_{coex} + y\left[C_{V_1} - C_{V_2} - \left(\frac{\partial P}{\partial V_1}\right)_T \left(\frac{\partial V_1}{dT}\right)^2_{coex} + \left(\frac{\partial P}{\partial V_2}\right)_T \left(\frac{\partial V_2}{dT}\right)^2_{coex}\right],$$

where $y = (\overline{V} - V_2)/(V_1 - V_2)$, and the indices 1 and 2 pertain to the coexisting phases. Thus, the reason for the appearance of a line of the maxima of the specific heat of a binary system on the T-V phase diagram in [1] is not the presence of impurities but external actions on the system.

We have shown earlier[3] that the inhomogeneity of the density over the height of the calorimeter (hydrostatic effect), due to the change of the hydrostatic pressure in measurement in a gravitational field, lead to the appearance of the maximum of the heat capacity of a binary system. It is natural to assume that the stirring employed in the experiments described in [1] does not eliminate the hydrostatic effect completely, and we can attempt to explain the results of the aforementioned experiments as being due to the influence of this effect during the stirring.

2. We shall consider the effect of stirring on the system in a gravitational field, using a simple idealized model. We assume that the stirring does not lead to a redistribution of the matter among the phases, i.e., to a noticeable heating of the system, but only equalizes the density of each phase in height. In this case the periodic operation of the stirrer[1)] causes the densities of the coexisting phases, after each stirring cycle (at $\tau_1 = 0$), to be homogeneous and equal to the densities on the coexistence curve, while in the intervals between the cycles

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[1)] In the experiments considered in [1], the frequency of stirring fluctuated from three to five times every three minutes, i.e., $\tau_1 = 1-0.6$ min.

(in the time interval $[0-\tau_1]$) there occurs in the system an isothermal relaxation of the distribution of the density towards the equilibrium distribution with respect to height in the gravitational field. The temperature of the calorimater in the time interval $[0-\tau_1]$ can be regarded as constant.[1] We shall assume henceforth that the main relaxation process at $0 \leq \tau \leq \tau_1$ is isothermal density relaxation, while the remaining thermodynamic quantities adjust themselves instantaneously to changes in density.

Numerous experiments[4] have shown that the time of equalization of mechanical disturbances near the critical point is of the order of several minutes, and does not depend strongly on the closeness to the critical point. Therefore, in a sufficiently narrow temperature interval near T_c, the time of isothermal relaxation of the density distribution with respect to the height, τ_0, can apparently be regarded as independent of $t = (T - T_c)/T_c$.

In our model, the action of the stirrer on the density distribution is equivalent to a decrease of the acceleration g due to the gravity (or the inhomogeneity scale l), from g_0 (or h) at $\tau \gg \tau_0$ to zero at $\tau = 0$, i.e., $g = g_0[1 - \exp(-\tau/\tau_0)]$ (or $l = h[1 - \exp(-\tau/\tau_0)]$). In perfect analogy with the procedure used in [5], we obtain from the classical equation of state[6] and from the hydrostatic condition the following equation for the distribution of the density in height as a function of the time:

for $t > 0$

$$\rho = \pm 2r\,\mathrm{sh}\frac{\varphi}{3}, \quad \mathrm{sh}\,\varphi = \frac{l}{h_0}, \quad r = \left(\frac{A|t|}{B}\right)^{1/2}; \tag{1a}$$

for $t < 0$

$$\rho = \pm 2r\,\mathrm{ch}\frac{\varphi}{3}, \quad \mathrm{ch}\,\varphi = \frac{l}{h_0} \quad \text{if} \quad |l| > h_0, \tag{1b}$$

$$\rho = \pm 2r\cos\frac{\varphi}{3}, \quad \cos\varphi = \frac{l}{h_0} \quad \text{if} \quad |l| < h_0, \tag{1c}$$

where $\rho = (\mathscr{P} - \mathscr{P}_c)/\mathscr{P}_c$, $t = (T - T_c)/T_c$, $p = (P - P_c)/P_c$, and $h = g_0\mathscr{P}_c(H - H_0)/P_c$ are the dimensionless density, temperature, pressure, and height measured from the meniscus; $A \equiv (\partial^2 p/\partial\rho\,\partial t)_c$, $B \equiv \frac{1}{2}(\partial^3 p/\partial\rho^3)_{tc}$ are the constants of the equation of state,[6] $l = h[1 - \exp(-\tau/\tau_0)]$ is the effective scale of the inhomogeneity of the density, and $h_0 = \frac{2}{3}B(A|t|/B)^{3/2}$ is the characteristic dimensionless height, determined by the closeness of the temperature to the critical value: when $|l/h_0| \gg 1$ the inhomogeneity of the density determines completely the result of the experiment, and when $|l/h_0| \ll 1$ it leads to corrections. The measured specific heat corresponds to

$$\bar{C} = -\frac{1}{\bar{\mathscr{P}} H_m \tau_1}\frac{d}{dT}\int_0^{\tau_1}\int_0^{H_m}[E(\mathscr{P}, T) + gH]\,\mathscr{P}\,d\tau\,dH, \tag{2}$$

where H_m and $\bar{\mathscr{P}}$ are the total height and the average density of matter in the calorimeter.

For the dimensionless specific heat $c_V = V_V T_c/P_c V_c$ we use the law considered in [7], in the form proposed by I. M. Lifshitz:

$$c_V = -\alpha\ln|t + \beta\rho^2| + \Delta, \tag{3}$$

where Δ is the finite part of the specific heat. The use of an equation with other critical indices for the isothermal compressibility and specific heat (see [8]) does not change the gist of the results of our calculations.

The calculation of the temperature of the jump of the specific heat and of the specific heat of the inhomogeneous system after stirring leads to results similar to those in [3,5], except that now the role of the inhomogeneity scale in the final formulas is played not by the total height of the vessel h_m, but by the time-averaged effective dimensionless inhomogeneity scale

$$\bar{l} = h_m\left\{1 - \frac{\tau_0}{\tau_1}\left[1 - \exp\left(-\frac{\tau_1}{\tau_0}\right)\right]\right\}$$

or

$$\bar{l} = h_m\frac{\tau_1}{2\tau_0} \quad \text{if} \quad \tau_1 < \tau_0.$$

The temperature of the transition through the coexistence curve (the jump of the specific heat) is, in accordance with [5],

$$t_j = -\frac{2B}{3A}\bar{\rho}^2\left(1 - \frac{3}{2B}\frac{\bar{l}}{|\bar{\rho}|^3}\right)$$
$$\text{if} \quad \frac{\bar{l}}{h_0} \ll 1 \text{ and } |\bar{\rho}| > \sqrt{3}\left(\frac{3\bar{l}}{2B}\right)^{1/3}, \tag{4}$$

$$t_j = -\frac{2B}{3A}\left(\frac{3\bar{l}}{B}\right)^{1/3}\left[|\bar{\rho}| - \frac{3}{4}\left(\frac{3\bar{l}}{B}\right)^{1/3}\right]$$
$$\text{if} \quad \frac{\bar{l}}{h_0} \gg 1 \quad \text{and} \quad \sqrt{3}\left(\frac{3\bar{l}}{2B}\right)^{1/3} > |\bar{\rho}| > \frac{3}{4}\left(\frac{3\bar{l}}{B}\right)^{1/3}, \tag{5}$$

$$t_j = 0 \text{ if } 0 \leq |\bar{\rho}| \leq \frac{3}{4}\left(\frac{3\bar{l}}{B}\right)^{1/3}, \tag{6}$$

where $\bar{\rho}$ is the average density of matter in the calorimeter.

The specific heat of the binary system has, as a result of the hydrostatic effect, a maximum at $|t| > (B/A)(3\bar{l}/2B)^{2/3}$.[3] The temperature of the maximum is[2]

$$t_{\max} = K\left(\frac{3\bar{l}}{2B}\right)^{2/3}\left[1 + M\left(\frac{3\bar{l}}{2B}\right)^{-2/3}\bar{\rho}^2\right], \tag{7}$$

where

$$K = -\frac{B}{A}\left(\frac{\sqrt{3}}{4}\frac{A\beta}{3A\beta - B}\right)^{2/3} \approx -0{,}3,$$

$$M = \frac{5}{36\sqrt{3}}\frac{A^2}{\alpha B}\left(\frac{4}{\sqrt{3}}\frac{3A\beta - B}{A\beta}\right)^{2/3} \approx 4\cdot 10^{-2}.$$

At the maximum points, the specific heat assumes values that depend on the average density and inhomogeneity scale:

$$\bar{c}_{\max} = \xi + \frac{2}{3}\alpha\ln\left(\frac{1}{\bar{l}}\right) - \gamma\left(\frac{3\bar{l}}{B}\right)^{-2/3}\bar{\rho}^2, \tag{8}$$

where

$$\xi = \Delta c_V{}^0 + \Delta - \alpha\ln\left|\frac{3}{4}\left(\frac{3A\beta - B}{A}\right)^{1/3}\left(\frac{\beta}{B}\right)^{2/3}\right|$$
$$-\frac{2}{3}\alpha \approx \Delta c_V{}^0 + \Delta + (10 \pm 5),$$

$$\gamma = \frac{4}{3}3^{1/3}\frac{A^2}{B}\left(1 - \frac{B}{3A\beta}\right)^{5/3} \approx 0,3,$$

Δc_V^0 is the jump of the specific heat in the homogeneous system. At $\bar{\rho} = 0$ we have

$$\bar{c}_{\max} = \text{const} + \text{const}\cdot\ln\left(\frac{1}{\bar{l}}\right). \tag{9}$$

Following [3], we can easily calculate the jump of the specific heat as a function of $\bar{\rho}$ and $\bar{l}$ for $\bar{l}/h_0 \ll 1$ and $\bar{l}/h_0 \gg 1$:

$$\Delta\bar{c} = \Delta c_V{}^0\left(1 - \frac{2}{3\sqrt{3}}\frac{\bar{l}}{h_0}\right) = \Delta c_V{}^0\left(1 - \frac{3}{B}\frac{\bar{l}}{|\bar{\rho}|^3}\right) \quad \text{if} \quad \frac{\bar{l}}{h_0} \ll 1; \tag{10}$$

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[2] To estimate the constants we use in this and in the preceding formulas the estimates given in [3]: $A = 3.8$, $B = 0.6$, $\alpha = 0.75$ and $\beta = 5.5 \times 10^{-2}$.

$$\Delta\bar{c}=\Delta c_V{}^0\sqrt{3}\left(\frac{h_0}{2\bar{l}}\right)^{1/3}=\Delta c_V{}^0\sqrt{\frac{2}{3}}\left(\frac{3\bar{l}}{B}\right)^{-1/6}\left[|\bar{\rho}|-\frac{3}{4}\left(\frac{3\bar{l}}{B}\right)^{1/3}\right] \quad (11)$$

$$\text{if} \quad \frac{\bar{l}}{h_0}\gg 1,$$

$$\Delta\bar{c}=0, \quad \text{if} \quad t=0 \text{ and } |\bar{\rho}|\leqslant\frac{3}{4}\left(\frac{3\bar{l}}{B}\right)^{1/3}. \quad (12)$$

In the case of continuous and sufficiently intense stirring, our model is not valid. With such stirring, however, there should appear in the system regions of density inhomogeneities, produced and maintained by the work of the stirrer. If the pressure in these regions changes with height linearity, then our formulas are valid also for this case, with $\bar{l}$ meaning a suitably averaged scale of the inhomogeneity regions. We note that in the direct vicinity of the critical point the surface tension and the heat of evaporation decrease, and continuous stirring can lead to a mutual dispersion of the phases and a to a redistribution of matter along the phases, and as a result also to an additional distortion of the features of the specific heat and to a decrease in the transition temperature.

3. Let us formulate some deductions from the foregoing formulas and compare our results with experiment.

A. As follows from (4)–(7), the inhomogeneity of the density in stirring causes the maximum and the jump of the specific heat at a given $\bar{\rho}$ to be separated in temperature, the line of the maxima is located inside the coexistence curve, and crosses it at $|\bar{\rho}| \approx \vartheta(3\bar{l}/2B)^{1/3}$, where ϑ is a combination of constants of Eqs. (4)–(7), (in order of magnitude, $\vartheta \approx 10$). When $|\bar{\rho}| > \vartheta(3\bar{l}/2B)^{1/3}$, the specific heat of a binary system has no maximum. There is a formal analogy between formula (9) and Onsager's well known result for the specific heat of a finite Ising lattice,[9] which of course is connected with our choice of the law (3) for the specific heat. This analogy, however, has a certain meaning if it is recognized that the inhomogeneity of the density over the calorimeter causes the phase transition to occur only in a very narrow interval of heights near h = 0, while in the remaining parts of the system the ordering parameter retains a nonzero value also at t > 0. The action of the hydrostatic effective decrease of the dimensions of the sample.

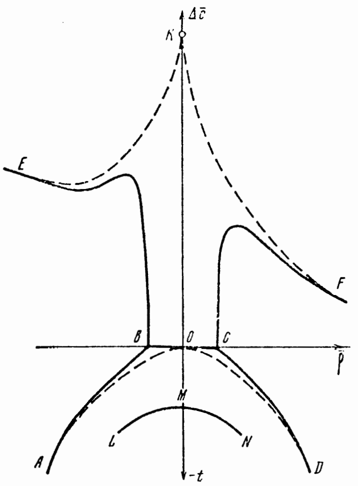

FIG. 1. Jump of the specific heat $\Delta\bar{c}$ and temperature of the transition (of the jump of the specific heat) as functions of the average density. Line EKF–jump $\Delta c_V{}^0$ in the absence of a gravitational field, EBCF–in a gravitational field. Transition temperature: in the absence of a gravitational field–AOD, in a gravitational field–ABCD. The line of the maxima of the specific heat of a binary system in a gravitational field–LMN. BC = $(3/2)(3\bar{l}B)^{1/3}$, OM–$K(3\bar{l}/2B)^{2/3}$.

	$\bar{\rho}\cdot 10^2$	$\Delta t\cdot 10^5$	$\bar{l}/h_m$	τ_1, min
From measurements of c_V [1].	4.8	3.2	0.2	1
	25	1.7	0.1	
From thermograms in accordance with the data of [19].	3.2	2.0	0.12	0.6
	5.3	1.4	0.04	
	−3.4	2.0	0.12	
	−6.6	1.4	0.07	

B. The temperature of the maximum of the specific heat at $\bar{\rho} = 0$ is not equal to the critical value, and amounts to $t_{\max} \sim 10^{-(4\pm 1)}$ at reasonable calorimeter heights. Assuming the temperature of the maximum as the critical temperature, we can obtain the law governing the variation of c_V near the critical point; this law differs appreciably from that observed if T_c is correctly chosen, since the character of the obtained relations depends very strongly on the choice of T_c.[2] In this connection we note that a decrease of the temperature conductivity of the medium on approaching to the critical point leads to an unlimited growth of the time of equalization of the thermal perturbation in the system as $t \to 0$ and $\rho \to 0$. The hydrostatic effect apparently should not lead to a deviation of the temperature T_τ corresponding to the maximum equalization time from T_c at a given $\bar{\rho}$. We therefore consider the use of T_τ for T_c in the analysis of the experimental results to be more correct than the identification of $T_{\max}$ with T_c.[3)]

Analogous results were drawn in [12] with respect to the determination of the Curie temperature of a real sample.

C. The jump of the specific heat due to the hydrostatic effect decreases and turns out to be dependent on the density. Inclusion of the next higher terms of the expansion in the equation of state[6] leads to a change in the dependence of $\Delta\bar{c}$ on $\bar{\rho}$ at densities far from critical, i.e., to the corrections that are the most significant in (10). The dependence of $\Delta\bar{c}$ on $\bar{\rho}$ with allowance for the next terms in the expansion, is shown schematically in Fig. 1. A similar $\Delta\bar{c}(\bar{\rho})$ dependence was observed in the experiments of Kerimov et al. (see, for example, [11]), on the basis of which they drew the incorrect conclusion that there is no jump of the specific heat at the critical point. For comparison, Fig. 1 shows (dashed) the $\Delta c_V(\bar{\rho})$ dependence for a homogeneous system.

D. Comparison of $\Delta t = t_{\max} - t_j$ from formulas (4), (5), and (7) with the results of calorimetric experiments with stirring[1] makes it possible to reconstruct the inhomogeneity scale $\bar{l}/h_m$ in the experiments.

The results of these calculations are listed in the table.[4)]

[3)] In [10] the critical temperature of xenon was assumed to be the temperature of the maximum of the specific heat. According to [10] $(T_\tau - T_{\max})/T_c \approx 2 \times 10^{-4}$. The choice of T_τ as the critical temperature, alters the deductions [10]. A similar remark can be made with respect to the experiments of Kerimov et al. [11]

[4)] The results of [1] for t_j and $t_{\max}$, used in these calculations, pertain to the case $\bar{l}/h_0 \ll 1$.

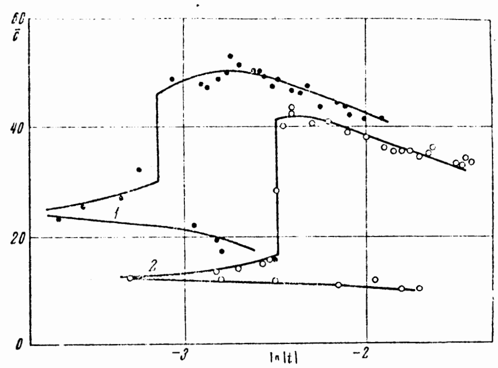

FIG. 2. Specific heat in experiments with stirring (τ_1 = 1 min): 1—$\bar{\rho}$ = 4.8 × 10^{-2}, O—experiment [4], solid lines—our calculation at $\bar{l}/h_m$ = 0.2 (τ_0 = 2 min); 2—ρ = 25 × 10^{-2}, O—experiment [1], solid lines—our calculation at $\bar{l}/h_m$ = 0.1 (τ_0 = 5 min). The values of $\bar{l}/h_m$ were determined from the position of the maximum of the specific heat in the experiments of [1].

We call attention to the decrease of $\bar{l}/h_m$ with increasing stirring frequency and with increasing distance from the critical point. The $\bar{c}(t, \rho)$ dependence and the values of the jump $\Delta\bar{c}$ of the specific heat, calculated with the inhomogeneity parameters $\bar{l}/h_m$ obtained from Δt, are in full agreement with experiment (see Fig. 2). From the ratios $\bar{l}/h_m$ we can estimate (of course, only in order of magnitude) the time of isothermal relaxation of the density $\tau_0 \sim \tau_1 h_m/2\bar{l}$. Estimates for different $\bar{\rho}$ lead to similar results: $\tau_0 \sim 2-15$ min. These estimates for τ_0 agree with the pressure equalization times near the critical point observed in the experiments of Krichevskiĭ and co-workers. Large equalization time (on the order of dozens of hours), observed in [1,4] are apparently the equalization times of the thermal perturbations, which increase strongly in connection with the sharp decrease of the coefficient of temperature conductivity near the critical point.

Reasonable estimates of $\bar{l}/h_m$ and τ_0, obtained from a comparison of our formulas with the experimentally obtained Δt, and also the agreement between the calculated values of $\bar{c}(t, \bar{\rho})$ and $\Delta\bar{c}$ with experiment,[1] give grounds for hoping that the explanation offered for the splitting of the maximum and the jump of the specific heat is correct.

4. A maximum of the specific heat below the transition point can result also from other external actions on the sample, for example the inhomogeneities connected with the preparation of the sample. The influence of such inhomogeneities on a second-order phase transition was investigated by Mikulinskiĭ, using a two-dimensional Ising model[13] and using the method of the theory of self-consistent fields,[14] for the case when the sample is cooled so rapidly that the impurities do not have time to enter in thermal equilibrium. These papers explain qualitatively the distortions of the singularity of the specific heat, observed in experiments with solid samples.[1, 15] The presence of impurities that are in thermodynamic equilibrium with the lattice cannot lead to a maximum of the specific heat below the transition point, but leads to a shift of the transition temperature and to a distortion of the singularity. The phase transition in a two-dimensional Ising lattice with such impurities was considered by Lushnikov.[16] In this model, the specific heat at the transition point remains finite and the temperature of the transition (of the maximum of the specific heat) T'_c shifts towards lower temperatures, but the distortion of the singularity at all concentrations is observed only in an exponentially narrow temperature region $(T'_c - T)/T'_c \lesssim 10^{-8}$ (in the experiments of Voronel' et al.[1] the singularity is distorted at $(T_{max} - T)/T_{max} \sim 10^{-3}$ when $\bar{\rho} = 0$).

In measurements of the specific heat c_V near the critical point, the gravitational field apparently is the main cause of the distortion of the singularity also in the presence of impurities. An appreciable hydrostatic effect is also observed near the critical point of a mixture.[17] At low impurity concentration, the inhomogeneity of the concentration in height is relatively small, but the density distribution over the height of the vessel changes, and it is not excluded that for certain systems the density inhomogeneity increases with increasing impurity concentration. Such an action of the impurities was noted in an interesting paper by Timrot and Shuĭskaya[18] for CO_2 with an air impurity.

In a homogeneous system, small impurities distort the singularity apparently only in a very narrow temperature interval near T_c (at $t \lesssim 10^{-8}$). Thus, at temperatures $t \sim 10^{-4}$ small impurities change the splitting of the maximum and of the jump and distort the singularity of c_V only via a change of the hydrostatic effect in the density. The presence of small impurities can be taken into account by renormalization of the constants in formulas (4)–(12), namely $A \rightarrow A + \text{const} \cdot \bar{x} \ln \bar{x}$, and $B \rightarrow B + \text{const} \cdot \bar{x}$, where const is a combination of thermodynamic derivatives that remain finite as $\bar{x} \rightarrow 0$. It is seen from (4)–(12) that the splitting of the maximum and of the jump of Δt is particularly sensitive to the values of the constants, since $3A\beta$ is close to B and a slight change of A and B leads to a strong change in the position of the maximum of the specific heat. The magnitude of the splitting of the maximum and of the jump can thus serve as a sensitive indicator of the purity of the substance. The linear dependence of the magnitude of the splitting of the maximum and of the jump of Δt on the impurity concentration $\bar{x}$ turns out to be valid, however, only for very small $\bar{x} \sim 10^{-2}$.

One more cause of the splitting of the maximum and of the jump may be the presence of temperature gradients over the height of the calorimeter, due to absence of equalization, since the temperature-conductivity coefficient of a substance near the critical point depends strongly on t and ρ.[5] The influence of small temperature gradients ($|\nabla t| \ll (dt/dp)_c$) on the results of the experiments is due mainly to the change of the hydrostatic effect. In our calculation we could take into account small temperature gradients in the system. This would lead, however, to a change of the constants in the equations; for example, allowance for a linear change of t over the height of the calorimeter $t = t_0 + bh$ leads to a renormalization of the constants A and B in Eqs. (4)–(12):

$$A \rightarrow \frac{A}{1 + b(dp/dt)_c}, \quad B \rightarrow \frac{B}{1 + b(dp/dt)_c}.$$

One must therefore exercise a certain caution in

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[5] This circumstance was pointed out to us by A. V. Voronel'.

comparing our formulas with experiment, since we can overestimate the influence of the hydrostatic effects with purer substances and with smaller temperature inhomogeneities when we determine the constants from the experimental data that are affected by the presence of impurities or temperature gradients in the calorimeter. We note in this connection that in recent experiments by Voronel' and Smirnov,[19] special measures were taken to decrease the impurities and the possible temperature gradients over the calorimeter. In these experiments no distortion was observed in the singularity of the specific heat up to $|t| \sim 10^{-5}$.

5. Second-order phase transitions in an external field have been relatively little investigated. In the case of a magnet in an external field, the inhomogeneity of the field over the sample, due, for example, to edge effects, can lead to an appreciable inhomogeneity of the magnetization and consequently to an additional distortion (compared with that investigated in [13, 14, 16]) of the singularity of the specific heat. All our formulas and the formulas of [3, 5] can, of course, be readily generalized to include cases of second-order phase transitions in external fields.

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255