EFFECT OF GRAVITY ON SPECIFIC HEAT MEASUREMENTS AND ON THE POSITION OF THE PHASE INTERFACE NEAR THE CRITICAL POINT

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A study is made of the effect of gravity on specific heat measurements in an experiment carried out without mixing of the fluid. The main contribution is determined not by the potential energy but by the dependence of the density, and therefore also of the specific internal energy, on height. The hydrostatic effect leads to the disappearance of the singularity at the critical point: in the immediate vicinity of this point the specific heat varies linearly with temperature, while in more remote regions the concept of a specific heat discontinuity between the one- and two-phase states remain valid. The specific heat maximum shifts into the two-phase region. The law of motion for the meniscus (or the location of maximum gradient in the one-phase region) due to a variation of temperature is also examined in detail. The calculations are compared with experiments carried out with and without mixing; the latter case is apparently consistent with the presence of a logarithmic singularity in the isochoric specific heat.

1. INTRODUCTION

As is well known, measurements of specific heat at constant volume C_V have demonstrated a logarithmic singularity when the critical point is approached which goes outside the framework of the classical theory of the critical point. In view of the great importance of such experiments, they were carried out on different substances for different degrees of proximity to the critical point; moreover, a careful analysis was made of the various factors which affect the result and the interpretation of calorimetric experiments.

The hydrostatic effect, i.e., a sharp increase in the inhomogeneity of the substance along the height of the vessel due to the infinite increase in compressibility, is one of the most important factors determining results of measurements near the critical point.

The effect of gravity on measurements of specific heat can be illustrated by an interesting problem[1]: it turns out that due to the presence of gravity the specific heat of a column of an ideal gas of height H defined as the derivative with respect to temperature of the sum of the internal and the potential energy is close to the specific heat at constant volume C_V for $H \ll RT/Mg$ or to the specific heat at constant pressure C_p for $H \gg RT/Mg$. The role of gravity is all the more significant near the critical point where for vessel heights of the order of 10 cm the values of the density of the ends of the vessel differ by 20–40%. Under such conditions even though a reduction of the height of the vessel by a factor of 2–3 does lead to interesting results[2], still it cannot appreciably eliminate the hydrostatic effect.

On the other hand, the continuous mixing of the fluid utilized in calorimetric measurements introduces perturbations into the state of the system which are difficult to take into account. Having in mind these difficulties and the aforementioned importance of calorimetric measurements near the critical point the problem of estimating quantitatively the influence of the hydrostatic effect on the measurements of specific heat appears to be of immediate interest.

Recently a number of papers has appeared[3,4] in which the experimenters measure the specific heat without mixing, and then try to establish the nature of the singularity by means of calculations. Although such a formulation of the problem is very interesting, nevertheless it is doubtful that it can lead to reliable results in view of the large number of adjustable parameters. We start with the existence of a logarithmic singularity in C_V at the critical point, calculate the effect of the gravitational field on the measured quantity in the absence of mixing and compare the results with experiment.

In order to solve the problem formulated above we utilize the results of our previous paper[5] on the distribution of the density of the fluid along the height of the vessel. In terms of dimensionless variables ($t = (T - T_c)/T_c$, $p = (P - P_c)/P_c$, $\rho = (\mathscr{P} - \mathscr{P}_c)/\mathscr{P}_c$, $h = \mathscr{P}_c gH/P_c$, where the height h is measured vertically upwards from the level of maximum density gradient, $h_0 = 2B(A|t|/B)^{3/2}/3$ is the characteristic height determined by the proximity of the temperature to the critical temperature) we have

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

$$t < 0: \qquad \rho = \begin{cases} \pm 2r\,\mathrm{ch}\dfrac{\varphi}{3}, & \mathrm{ch}\,\varphi = \dfrac{h}{h_0} \quad \text{for} \quad |h| > |h_0|, \\ \pm 2r\cos\dfrac{\varphi}{3}, & \cos\varphi = \dfrac{h}{h_0} \quad \text{for} \quad |h| < |h_0|. \end{cases} \tag{1.1}$$

For the average density

$$\bar{\rho}_h = \frac{1}{h}\int_0^h \rho\, dh$$

we obtain from (1.1) for $t < 0$:

$$\bar{\rho}_h = \begin{cases} -\frac{3}{4}\left(\frac{3h}{B}\right)^{1/3}\left[1+2^{1/3}\left(\frac{h_0}{h}\right)^{2/3}+\ldots\right] & \text{for } |h| \gg |h_0|, \\ \pm\left(-\frac{3At}{B}\right)^{1/2}\left[1+\frac{1}{6\sqrt{3}}\frac{h}{h_0}+\ldots\right] & \text{for } |h| \ll |h_0|; \end{cases}$$

for $t > 0$: (1.2)

$$\bar{\rho}_h = \begin{cases} -\frac{3}{4}\left(\frac{3h}{B}\right)^{1/3}\left[1-2^{1/3}\left(\frac{h_0}{h}\right)^{2/3}+\ldots\right] & \text{for } |h| \gg |h_0|, \\ -\frac{h}{2At} & \text{for } |h| \ll |h_0|. \end{cases}$$

We make a few remarks relative to equations (1.1), (1.2).

1. In obtaining these formulas the equation of state for the medium near its critical point was used in the form

$$\left(\frac{\partial p}{\partial \rho}\right)_t = At + B\rho^2, \quad A = \left(\frac{\partial^2 p}{\partial \rho\, \partial t}\right)_c, \quad B = \frac{1}{2}\left(\frac{\partial^3 p}{\partial \rho^3}\right)_c, \tag{1.3}$$

i.e., the singular part of the free energy which according to[6] has the form[1)]

$$F_{\text{sing}} = \frac{\alpha t^2}{2}\ln|t+\beta\rho^2+\ldots| + t^2 h\left(\frac{t}{\rho^2}\right). \tag{1.4}$$

was not taken into account.

Taking into account the additional singular term (1.4) in the equation of state (1.3) reduces to the replacement of the coefficient A by the following expression

$$A \to A + \frac{\alpha\beta t}{t+\beta\rho^2} + \frac{2t^2}{\rho^4}h'\left(\frac{t}{\rho^2}\right). \tag{1.5}$$

Similar additional terms enter into the other thermodynamic derivatives.

Mathematically such a renormalization of coefficients is completely natural and is associated with the fact that the limiting value of a function of two variables at a singular point depends on the path taken to approach this point. At the same time, all the additional terms which are functions of the ratio t/ρ^2 are finite for all values of this parameter (the properties of the function $h(t/\rho^2)$ have been investigated in reference[6]), can be expanded in power series, and taking them into account reduces to a renormalization of the constants and to small corrections. One should only keep in mind that in making comparisons with experiment the parameter A determined from relations containing different derivatives can turn out to have different values.

Thus, the singular part of the free energy (1.4) which completely determines the singularity in C_V and in a number of other derivatives of the free energy with respect to the temperature, for example, the adiabatic velocity of sound, is at the same time of little significance for the equation of state, i.e., for the derivatives of the free energy with respect to the volume.

2. From formulas (1.2) follows the existence of a flat region on the isothermals beyond the critical one. The experimental determination of the PVT-relations for $T > T_c$ led to the existence of such a flat region, for example, in a number of papers by Canadian physicists.

If the sensitivity of the apparatus which is used to measure the pressure is equal to $\pm p'$, then independently of the height of the piesometer an indeterminacy arises in the position of the maximum gradient of the density with respect to the height (in terms of our variables $dh = -dp$) $|h'| = |p'|$. Then for the flat region $\Delta\rho$ on the isothermal we have

$$\Delta\rho = \begin{cases} \frac{|h'|}{At} & |h'| < |h_0|, \\ \frac{3}{2}\left(\frac{3|h'|}{B}\right)^{1/3}\left[1-2^{1/3}\left(\frac{h_0}{h'}\right)^{2/3}\right] & |h'| > |h_0|. \end{cases} \tag{1.6}$$

The magnitude of the flat region becomes small (less than 0.2% of $\mathscr{P}_c$) for $|t| > |h'| \times 10^{-2}$, i.e., (for $P_c \approx 50$ atm, $T_c \approx 300°$K, $P' \sim 1$ mm Hg) for temperatures $|t| > 10^{-3}$ or $T - T_c > 0.3°$K.

We note that also for the analysis of the shape of the coexistence curve near the critical point one should take into account together with the inhomogeneity parameter H_m and the correlation radius r_c (cf., reference[5]) also the existence of an indefiniteness h' in the position of the meniscus.

2. MOTION OF THE INTERFACE BETWEEN THE PHASES ALONG THE HEIGHT OF THE VESSEL

At temperatures below critical one measures the specific heat of a heterogeneous system for the calculation of which it is necessary to evaluate beforehand the position of the interface between the phases (the meniscus) and its motion along the height of the vessel as the temperature t varies for a given density of filling[2)] $\bar{\rho}$.

We denote the distance from the bottom of the vessel to the meniscus by h, and from the meniscus to the top of the vessel by h_+; correspondingly we denote the average densities in the region $(0, h_+)$ by ρ_+ and in the region $(h_-, 0)$ by ρ_-. We have the two obvious relations:

$$h_+ - h_- = h_M, \quad \bar{\rho} h_M = \rho_+ h_+ - \rho_- h_-, \tag{2.1}$$

from which follow the generalized—taking the hydrostatic effect into account—laws of the lever

$$h_- = \frac{\bar{\rho} - \rho_+}{\rho_+ - \rho_-}h_M, \quad h_+ = \frac{\bar{\rho} - \rho_-}{\rho_+ - \rho_-}h_M. \tag{2.2}$$

These formulas contain the parameter $\bar{\rho}$—the average filling density for the vessel.

In the absence of the hydrostatic effect or in the case when mixing completely eliminates this effect in each phase it is obvious that

$$|\rho_-| = |\rho_+| = |\rho_{\text{ves}}| = (-3At/B)^{1/2},$$

$$h_- = -\frac{h_M}{2}\left(1 + \frac{\bar{\rho}}{|\rho_{\text{ves}}|}\right) = -\frac{h_M}{2}\left[1 + \bar{\rho}\Big/\left(-\frac{3At}{B}\right)^{1/2}\right], \tag{2.3}$$

[1)]The argument of the logarithm is here written in a simpler form than in [6] where the condition that this expression should be positive was automatically guaranteed by the introduction of still another constant. I.M. Lifshitz has shown that the argument of the logarithm in formula (1.4) is guaranteed to be positive for homogeneous states if the curve $t + \beta\rho^2$ is a spinodal.

[2)]I.R. Krichevskiĭ brought to our attention the independent interest of experiments on the visual observation of the motion of the meniscus with a change in temperature for different amounts of substance in the vessel. Such experiments can enable one to determine certain important characteristics of the substance near its critical point, for example, a quantity which is difficult to measure – the critical value of the density. In these experiments one should carefully observe the time for the establishment of equilibrium of density along the height of the vessel, since formulas for the case of a completely established distribution of density and for the case when the hydrostatic effect is eliminated turned out to be quite different.

i.e., in the immediate vicinity of the critical point the meniscus undergoes acceleration: $dh/dt \to \infty$.

In order to calculate the motion of the meniscus in the presence of the hydrostatic effect we utilize formulas (1.2) for the average density which have different form for $|h_0| > |h_\pm|$ and $|h_0| < |h_\pm|$. Correspondingly we consider different cases realized for a meniscus which is situated near the center or near the top (bottom) of the vessel.

1. $|h_0| > |h_\pm|$. Solving (2.2) and (1.2) simultaneously we obtain

$$h_- = -\frac{h_M}{2}\left\{1 + \bar{\rho}\left[\left(-\frac{3At}{B}\right)^{1/2} - \frac{h_M}{4At}\right]^{-1}\right\},$$

$$\frac{dh_-}{dt} = -\frac{A\bar{\rho}}{6\sqrt{3}}\left|\frac{h_M}{h_0}\right|. \tag{2.4}$$

2. $|h_0| < |h_\pm|$. In this case we solve (1.2) and (2.2) approximately assuming that $h_- = -h_M/2 + \xi$, $h_+ = h_M/2 + \xi$ and $\xi \ll h_M/2$, i.e., $\bar{\rho} < (3h_M/2B)^{1/3}$ (meniscus near the middle of the vessel). Linearizing (2.2) with respect to ξ, we obtain

$$h_- = -\frac{h_M}{2}\left\{1 + \bar{\rho}\left[\left(\frac{3h_M}{2B}\right)^{1/3}\left(1 + \left(\frac{h_0}{h_M}\right)^{2/3}\right)\right]^{-1}\right\},$$

$$dh_-/dt = -A\bar{\rho}/3. \tag{2.5}$$

3. $|h_+| < |h_0|$, $|h_-| > |h_0|$. Here also we solve (2.2) and (1.2) approximately assuming that $h_- = -h_M + \xi$, $h_+ = \xi$, $\xi \ll h_M$ (meniscus near the top of the vessel). Finally we obtain

$$h_- = -h_M\left\{1 + \frac{\bar{\rho} - {}^3/_4(3h_M/B)^{1/3}[1 + 2^{1/3}(h_0/h_M)^{2/3}]}{(-3At/B)^{1/2} + (3h_M/B)^{1/3}}\right\}$$

$$dh_-/dt = -2A\bar{\rho}/3. \tag{2.6}$$

4. $|h_+| > |h_0|$, $|h_-| < |h_0|$ (meniscus near the bottom of the vessel). In analogy with the preceding case we obtain

$$h_- = -h_M\frac{\bar{\rho} + {}^3/_4(3h_M/B)^{1/3}[1 + 2^{1/3}(h_0/h_M)^{2/3}]}{(-3At/B)^{1/2} + (3h_M/B)^{1/3}},$$

$$dh_-/dt = -2A\bar{\rho}/3. \tag{2.7}$$

Formulas (2.4)—(2.7) give the solution to the problem of the motion of the meniscus for a given filling $\bar{\rho}$ as a function of t. If $\bar{\rho} = 0$ (critical value) then the meniscus is situated at the middle of the vessel and does not move as the temperature varies. For $\bar{\rho} \neq 0$ the meniscus moves upwards, if $\bar{\rho} > 0$, and downwards, if $\bar{\rho} < 0$, and leaves the vessel for $|\bar{\rho}| > |\bar{\rho}_{ves}|$ through the bottom ($\bar{\rho} < 0$) or through the top ($\bar{\rho} > 0$), i.e., only one phase remains in the vessel. For comparatively large values of $|t|$ ($|h_0| \gg |h_M|$) its motion is described by formulas (2.4). Further, as $t \to 0$ the formulas (2.5) is operative, if $|\bar{\rho}| < (3h_M/2B)^{1/3}$, or alternatively formulas (2.6), (2.7), if $|\bar{\rho}| > (3h_M/2B)^{1/3}$.

All these results have been obtained from the equation of state (1.3). Taking into account higher order terms in this equation, specifically $Ct\rho + K\rho^3$, leads to an asymmetry in the coexistence curve [8], to an asymmetry in the flat regions (1.6) on the isothermals, and also to a motion of the meniscus with temperature even for $\bar{\rho} = 0$. The effect of these terms on the shape of the coexistence curve has been taken into account in the work of one of the authors [8]. In a completely analogous manner one can take into account corrections in formula (1.1) for the hydrostatic effect, in (1.2) for the average density and, finally, in formulas for the motion of the meniscus. A study of the motion of the meniscus can serve as a method for determining critical parameters and the coefficients in the equation of state of the fluid near the critical point.

In future we shall also require the knowledge of the law of motion of the level of maximum density gradient for temperatures above the critical temperature ($t > 0$). We give the simultaneous solutions of (1.2) and (2.2) obtained by an analogous method.

1. $|h_0| > |h_\pm|$ ("far" from the critical point):

$$h_- = -\frac{h_M}{2}\left[1 + \frac{2\bar{\rho}At}{h_M}\right],$$

$$dh_-/dt = -A\bar{\rho}. \tag{2.8}$$

2. $|h_0| < |h_\pm|$ ("near" the critical point, the maximum gradient is situated near the middle of the vessel):

$$h_- = -\frac{h_M}{2}\left\{1 + \bar{\rho}\left[\left(\frac{3h_M}{2B}\right)^{1/3}\left(1 - \left(\frac{h_0}{h_M}\right)^{2/3}\right)\right]^{-1}\right\},$$

$$dh_-/dt = -A\bar{\rho}/3. \tag{2.9}$$

3. $|h_0| > |h_+|$, $|h_0| < |h_-|$ (the maximum gradient is situated at the top of the vessel):

$$h_- = -h_M\left\{1 + \frac{\bar{\rho} - {}^3/_4(3h_M/B)^{1/3}[1 - 2^{1/3}(h_0/h_M)^{2/3}]}{(3h_M/B)^{1/3}[1 - (h_0/2h_M)^{2/3}]}\right\},$$

$$dh_-/dt = -2A\bar{\rho}/3. \tag{2.10}$$

4. $|h_0| < |h_+|$, $|h_0| > |h_-|$ (maximum gradient is situated near the bottom of the vessel):

$$h_- = -h_M\frac{\bar{\rho} + {}^3/_4(3h_M/B)^{1/3}[1 - 2(h_0/2h_M)^{2/3}]}{(3h_M/B)^{1/3}[1 - (h_0/2h_M)^{2/3}]},$$

$$dh_-/dt = -2A\bar{\rho}/3. \tag{2.11}$$

We emphasize once again that in studying the motion of the meniscus near the critical point an insufficiently long period of waiting for the establishment of equilibrium can lead to a situation intermediate between (2.3) and (2.4)—(2.11), or to one which is even closer to (2.3) than to (2.4)—(2.11).

3. SPECIFIC HEAT OF THE SYSTEM IN THE PRESENCE OF GRAVITY

The total energy of a fluid situated in a gravitational field in a vessel of height H with a mean filling density $\bar{\mathscr{P}}$ is equal to

$$E = \int_0^{z_0} \mathscr{P}'(E' + gz)\,dz + \int_{z_0}^{H} \mathscr{P}''(E'' + gz)\,dz. \tag{3.1}$$

Here we have introduced the coordinate of the maximum density gradient with respect to the height of the vessel z_0 (in the case of a two-phase system z_0 is the position of the meniscus); $\mathscr{P}''$ and $\mathscr{P}'$ are the densities of the upper and the lower phases. The effect of the gravitational field in addition to the potential energy $\mathscr{P}_{gz}$ in (3.1) also manifests itself in the z-dependence of $\mathscr{P}(z)$, and consequently also of $E(z)$.

The specific heat of such a system is equal to

$$C = \frac{1}{\mathscr{P}H}\frac{d}{dT}\Big[\int_0^{z_0}\mathscr{P}'(E'+gz)dz+\int_{z_0}^{H}\mathscr{P}''(E''+gz)dz\Big]. \quad (3.2)$$

In differentiating in (3.2) one must take into account the fact that z_0 is a function of the temperature and that the total mass of the fluid in the system is constant:

$$\int_0^H \mathscr{P}dz = \text{const.}$$

Expanding the internal energy in a series near the critical point

$$E = E_c + \left(\frac{\partial E}{\partial V}\right)_c (V - V_c) + \left(\frac{\partial^2 E}{\partial V^2}\right)_c \frac{(V-V_c)^2}{2} + \ldots,$$

we obtain after a simple calculation

$$C = \frac{1}{\mathscr{P}H}\Big\{\int_0^{z_0}\Big[\mathscr{P}'C_v' - \frac{1}{\mathscr{P}'}\left(\frac{\partial^2 E'}{\partial V^2}\right)_c (V' - V_c)\left(\frac{\partial \mathscr{P}'}{\partial T}\right)_z$$

$$+ gz\left(\frac{\partial \mathscr{P}'}{\partial T}\right)_z\Big]dz + \int_{z_0}^{H}\Big[\mathscr{P}''C_v'' - \frac{1}{\mathscr{P}''}\left(\frac{\partial^2 E''}{\partial V^2}\right)_c (V'' - V_c)\left(\frac{\partial \mathscr{P}''}{\partial T}\right)_z$$

$$+ gz\left(\frac{\partial \mathscr{P}''}{\partial T}\right)\Big]dz + (\mathscr{P}_0' - \mathscr{P}_0'')gz_0\frac{dz_0}{dT}\Big\}. \quad (3.3)$$

The last term in (3.3) is the change in the potential energy dependent on the temperature associated with the motion of the meniscus ($\mathscr{P}_0''$ and $\mathscr{P}_0'$ are the densities of the upper and the lower phases at the interface). If the system is a single-phase one, then $\mathscr{P}_0' = \mathscr{P}_0''$ and this term is equal to zero.

From (3.3) it is easy to obtain the discontinuity in the specific heat at the critical point in going over from a two-phase system into a single-phase one in the absence of gravity. In this case $g = 0$, E and P do not depend on the height within the boundaries of each phase. Then $\mathscr{P}' = \mathscr{P}'_{ves}$, $\mathscr{P}'' = \mathscr{P}''_{ves}$. Utilizing the equation of the coexistence curve (in terms of dimensionless variables) $\rho_{ves} = \pm(-3At/B)^{1/2}$ we easily obtain from (3.3) for all points of the coexistence curve, except for the critical point, $\Delta c_V = c_{Vhet} - c_{Vhom} = 3A^2/2B$ (here we have introduced the dimensionless specific heat $c = CT_c/P_cV_c$)—a well known result[7]. It is of interest that the critical point turns out to be distinctive. For example, for $c_{Vsing} = -\alpha \ln|t + \beta\rho^2|$ in the homogeneous region for $\rho = 0$ we have $c_{Vsing} = -\alpha \ln|t|$, while in the heterogeneous region we have $c_{Vsing} = -\alpha \ln|t + \beta\rho_{ves}(t)|$, i.e.,

$$\Delta c_v(T_c) = \frac{3A^2}{2B} - \alpha \ln\left|1 - \frac{3A\beta}{B}\right|.$$

At the same time, both from (3.3) and also from simple physical considerations it is clear that the existence of gravity in the case of high compressibility of substance in the vessel essentially changes the picture of this phenomenon. If previously in the appearance of the new phase in the vessel near the critical point the small value of the latent heat of vaporization ($q \sim |t|^{1/2}$) was compensated by the large amount of the appearing phase of different density ($d\rho_{ves}/dt \sim |t|^{-1/2}$ over the whole volume), now the hydrostatic effect leads to a strong inhomogeneity over the whole vessel and $d\rho/dt \to \infty$ only over a narrow layer near the meniscus, while for the derivative of the average density of each phase $d\bar{\rho}_\pm/dt$ the critical point is not distinguished in any way. A decrease in the latent heat of vaporization as the critical point is approached leads in the presence of the hydrostatic effect to the disappearance of the discontinuity of the specific heat of the critical point.

Transition to dimensionless variables introduced in Sec. 1 enables us to utilize the equation of state (1.3) near the critical point and to take into account in the simplest possible manner the dependence of z_0, $\mathscr{P}(z)$ and $(\partial\mathscr{P}/\partial T)$ on the average filling density.

In terms of these variables after a simple calculation formula (3.3) can be reduced to the form

$$\bar{c} = \frac{1}{h}\Big[\int_h^{h_+} c_v dh + \int_{h_-}^{h_+}(A\rho + h)\left(\frac{\partial\rho}{\partial t}\right)_h dh + \frac{dh_-}{dt}\int_{h_-}^{h_+}(A\rho + h)\left(\frac{\partial\rho}{\partial h}\right)_t dh\Big]. \quad (3.4)$$

The height as before is measured from the point of maximum density gradient. In evaluating $\bar{c}$ for $\bar{\rho} = 0$ the last term in (3.4) is equal to zero, since $dh/dt = 0$, i.e., z_0 does not move.

We shall in future be interested in the following ranges of variation of heights: for $\bar{\rho} = 0$:

1) $|h_\pm| \ll h_0$—"far" from the critical point,

2) $|h_\pm| \gg h_0$—in the immediate vicinity of the critical point; for $\bar{\rho} \neq 0$:

1) $|h_\pm| \ll |h_0|$—"far" from the critical point,

2) $|h_\pm| \gg |h_0|$—close to the critical point,

3) $|h_-| \gg |h_0| \gg |h_+|$ or 4) $|h_-| \ll |h_0| \ll |h_+|$—near the coexistence curve.

The regions 1—4 on the phase diagram are schematically shown in Fig. 1.

Far from the critical point the regions 1 and 3—4 overlap since starting with certain values of t we have $|h_0| \gg |h_M|$ and in the vessel we always have $|h_\pm| \ll |h_0|$. Near the critical point the difference in cases 2 and 3—4 will manifest itself by the fact that for $\bar{\rho} = 0$ the last term in (3.4) associated with the motion of the meniscus with varying t is absent. The behavior of $\bar{c}$ will be determined both in case 2 and also in cases 3—4 by the parts of the vessel with $|h| \gg |h_0|$.

Since, as has been shown in Sec. 1, dh_-/dt depends only weakly on the proximity to the critical point, the difference between cases 2 and 3—4 will not be great near the critical point. Depending on the filling density in the vessel one can have with decreasing t the successive appearance of cases 1—2 ($|\bar{\rho}| < 3(3h_M/B)^{1/3}/4$, 1—2—3 or 1—2—4 ($|\bar{\rho}| < (3h_M/2B)^{1/3}$) and 1—3 or 1—4 ($|\bar{\rho}| > (3h_M/2B)^{1/3}$).

We now go on to evaluate the specific heat for different specific cases noting that since near the critical point one can neglect the variation of the regular part Δ compared to the logarithmic term, then for c_V for each

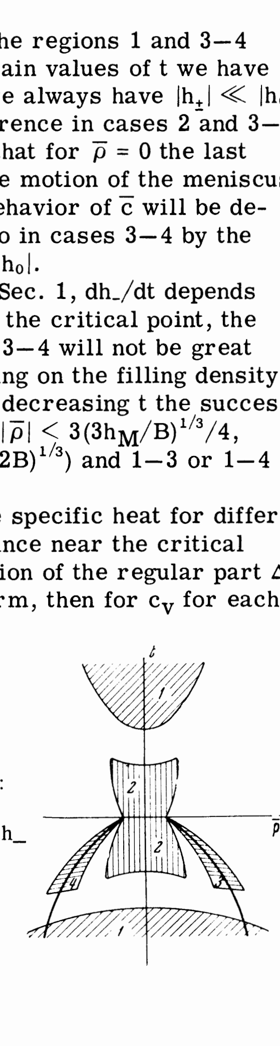

FIG. 1. Position of the regions in the ρ, t-phase diagram near the critical point: $1-|h_\pm| \ll |h_0|$, $2-|h_\pm| \gg |h_0|$, $3-|h_-| \gg |h_0| \gg |h_+|$, $4-|h_-| \ll |h_0| \ll |h_+|$ (h_+, h_- are defined by (2.2)).

phase we assume

$$c_v = -\alpha \ln|t+\beta\rho^2| + \Delta, \tag{3.5}$$

where Δ is the regular part of the specific heat. All the derivatives appearing in (3.4) can be easily obtained from the equations of Sec. 1.

First of all we note that in all the cases of interest to us we can neglect in the integrals of formula (3.4) the additive term h compared to $A\rho$. Physically this means that the gravitational field affects the specific heat being measured much more strongly not directly through the potential energy ($\mathscr{P}gz$ in (3.1)), but due to the inhomogeneity in the density P(z) brought about by the gravitational field, and due to the dependence of the internal energy on the height of the vessel ($E[T, \mathscr{P}(z)]$ in (3.1)).

The remaining four terms in (3.4) are associated with the dependence of c_V on the height, with the redistribution of the density along the height for a motionless meniscus and with the redistribution of density due to the motion of the meniscus.

We consider different cases for temperatures greater in the critical temperature ($t > 0$).

1. $|h_\pm| < |h_0|$ ("far" from the critical point, $t > t_0 = (B/A)\cdot(3h_M/2B)^{2/3}$). After straightforward calculations utilizing the values of $h_\pm$ from (2.4), we obtain

$$\bar{c} = -\alpha\ln\left|t+\beta\bar{\rho}^2+\beta\frac{h_M^2}{4A^2t^2}\right| + \frac{A\bar{\rho}^2}{t}+\Delta+O\left(\frac{h_M^2}{h_0^2}\right). \tag{3.6}$$

Thus, "far" from the critical point ($t > t_0 = 10^{-4}\,H_M^{2/3}$, where H_M is expressed in centimeters[5]) the specific heat remains logarithmic.

2. $|h_\pm| > |h_0|$ ("near" the critical point, $t < t_0$, the maximum density gradient is situated near the middle of the vessel). For this case we have

$$\bar{c} = \frac{A^2}{B}+\frac{2}{3}\alpha\left(1-\frac{2}{3}\bar{\rho}\right)-\alpha\ln\left[\beta\left(\frac{3h_M}{2B}\right)^{2/3}\right]+\Delta$$
$$-\frac{3A^2}{B}\left(1+\frac{\alpha B^2}{\beta A^3}\right)\left(1-\frac{2A\beta}{B}\right)\left(\frac{h_0}{h_M}\right)^{2/3}. \tag{3.7}$$

For $\rho = 0$ we have

$$\bar{c} = \frac{A^2}{B}+\frac{2}{3}\alpha-\alpha\ln\left[\beta\left(\frac{3h_M}{2B}\right)^{2/3}\right]+\Delta-\frac{3A^2}{B}\left(1+\frac{\alpha B^2}{\beta A^3}\right)\left(1-\frac{2A\beta}{B}\right)\left(\frac{h_0}{h_M}\right)^{2/3} \tag{3.8}$$

and at the critical point itself we have

$$\bar{c} = \frac{A^2}{B}+\frac{2}{3}\alpha+\Delta-\alpha\ln\left[\beta\left(\frac{3h_M}{2B}\right)^{2/3}\right].$$

As can be seen from (3.7) and (3.8), near the critical point the hydrostatic effect leads to a linear (and not to a logarithmic) dependence of the measured specific heat on the temperature. At the critical point itself the specific heat remains finite, while its value depends on the height of the vessel.

The cases $|h_+| < |h_0|$, $|h_-| > |h_0|$ and $|h_+| > |h_0|$, $|h_-| < |h_0|$ for $t > 0$ are of no interest, since the whole coexistence curve now lies at $t < 0$.

We now go over to studying the specific heat at temperatures lower than the critical temperature.

For the case $|h_\pm| \geq |h_0|$ ($|t| < |t_0|$, meniscus at the middle of the vessel):

$$\bar{c} = \frac{A^2}{B}+\frac{2}{3}\alpha\left(1-\frac{2}{3}\bar{\rho}\right)-\alpha\ln\left[\beta\left(\frac{3h_M}{2B}\right)^{2/3}\right]$$
$$+\Delta-\frac{3A^2}{B}\left(1+\frac{\alpha B^2}{\beta A^3}\right)\left(1-\frac{2A\beta}{B}\right)\left|\frac{h_0}{h_M}\right|^{2/3}. \tag{3.9}$$

For temperatures which are "far" from the critical temperature, $|h_\pm| < |h_0|$ ($|t| > |t_0|$, the meniscus near the middle of the vessel):

$$\bar{c} = \frac{3A^2}{2B}-\alpha\ln\left|1-\frac{3A\beta}{B}\right|+\Delta-\alpha\ln|t|$$
$$-\left(\frac{\sqrt{3}}{6}\frac{\alpha\beta A}{(3A\beta-B)}-\frac{A\bar{\rho}^2}{12\sqrt{3}t}\right)\left|\frac{h_M}{h_0}\right|. \tag{3.10}$$

For $t < 0$ it is also of interest to consider the cases $|h_-| > |h_0| > |h_+|$ and $|h_-| < |h_0| < |h_+|$, to the extent to which they correspond to an approach to the coexistence curve. For $|h_-| > |h_0| > |h_+|$ (the meniscus is situated at the top of the vessel, the filling density is close to the fluid density on the coexistence curve) after simple calculations taking into account the fact that $|h_-| \gg |h_+|$, we obtain

$$\bar{c} = \frac{A^2}{B}+\frac{2}{3}\alpha\left(1-\frac{2}{3}\bar{\rho}\right)-\alpha\ln\left[\beta\left(\frac{3h_M}{2B}\right)^{2/3}\right]+\Delta$$
$$-\frac{3A^2}{B}\left(1+\frac{\alpha B^2}{\beta A^3}\right)\left(1-\frac{2A\beta}{B}\right)\left|\frac{h_0}{h_M}\right|^{2/3}+h_+\left(1-\left|\frac{h_0}{h_M}\right|^{2/3}\right). \tag{3.11}$$

Here we have

$$h_+ = \left\{\bar{\rho}-\frac{3}{4}\left(\frac{3h_M}{B}\right)^{1/3}\left[1-2\left(\frac{h_0}{2h_M}\right)^{2/3}\right]\right\}\cdot$$
$$\times\left[\left(-\frac{3At}{B}\right)^{1/2}+\left(\frac{3h_M}{B}\right)^{1/3}\right]^{-1}h_M.$$

On the coexistence curve itself we have $h_+ = 0$ and $\bar{\rho} = \bar{\rho}_{\text{ves}}$

$$\bar{c} = \frac{A^2}{B}+\frac{2}{3}\alpha\left(1-\frac{2}{3}\bar{\rho}_{\text{ves}}\right)-\alpha\ln\left[\beta\left(\frac{3h_M}{2B}\right)^{2/3}\right]+\Delta$$
$$-\frac{3A^2}{B}\left(1+\frac{\alpha B^2}{\beta A^3}\right)\left(1-\frac{2A\beta}{B}\right)\left|\frac{h_0}{h_M}\right|^{2/3}.$$

The calculation is completely analogous for the case $|h_+| > |h_0| > |h_-|$ (the meniscus is at the bottom of the vessel, the filling density is close to the density of the gas on the coexistence curve).

From a comparison of formulas (3.8) and (3.9) it can be seen that the specific heats of the two- and the one-phase systems in approaching the critical point become equal; the discontinuity in the specific heat in passing through the critical point is equal to zero. With an accuracy up to terms written out in (3.11) there is no discontinuity in the specific heat not only at the critical point itself, but also near it in crossing over the coexistence curve.

"Far" from the critical point ($|h_0| > |h_\pm|$) the difference between the specific heats of the two- and the one-phase regions is determined by formulas (3.6) and (3.10). From these formulas it can be seen that for filling densities equal to or sufficiently close to the critical density the difference in the specific heats in the first approximation is equal to

$$(\Delta c_v)_{\text{crit}} = \frac{3A^2}{2B}-\alpha\ln\left|1-\frac{3A\beta}{B}\right|.$$

For densities "far" from the critical density, i.e., for

$$|\bar{\rho}| > \left(\frac{3h_M}{2B}\right)^{1/3}\left(\frac{B}{A\beta}\right)^{1/2}\left(\frac{h_0}{h_M}\right)^{1/3}$$

this difference is close to $3A^2/2B$. In order that in agreement with experiment the discontinuity found at the critical point $(\Delta c_V)_{\text{crit}}$ would be greater than the discontinuity far from it ($3A^2/2B$) we must have $0 < 3A\beta/B < 2$.

The distribution of density along the height of the vessel for the case $|h_0| > |h_\pm|$ in the first approximation coincides with the one which holds in the case of mixing of fluid (cf., the discussion of formula (3.3)).

4. DISCUSSION OF RESULTS

As can be seen from the formulas exhibited in Sec. 3 the gravitational field exerts a significant influence on the measurement of specific heat at the critical point. It turns out that the principal role is played not by the change in the potential energy of the system in an external field, but by the redistribution brought about by the field of the density along the height of the vessel which leads to a change in the specific internal energy[3)].

The value of the specific heat at the critical point remains finite. Physically such a "cutoff" of the singularity is associated with the small height of that layer of the fluid where the density is equal to the critical density compared to the noncritical layers. In the immediate vicinity of the critical point the temperature dependence of specific heat is not logarithmic but linear. From a comparison of formulas (3.7) and (3.9) it can be seen that at the critical point not only do the values of the specific heat themselves coincide but also of their derivatives, i.e., the critical temperature is now not distinguished in any manner.

The maximum in the specific heat lies in the two-phase region and is situated at temperatures $|h_0| \gtrsim |h_M|$, i.e., $t \gtrsim t_0$ ($t \gtrsim 10^{-4} H_M^{2/3}$, where H_M is expressed in centimeters). Indeed, from (3.9)—(3.11) it can be seen that the specific heat in the two-phase system increases for $|h_0| \gg |h_M|$ and decreases for $|h_0| < |h_M|$. At the same time everywhere in the one-phase region the specific heat remains a monotonic function which increases as the critical point is approached.

Figure 2 shows experimental data for calorimeters of two heights (8 and 2.5 cm) for $\bar{\rho} = 0$ taken from[2]. An obvious qualitative agreement exists between the formulas obtained in Sec. 3 and experiment. For a quantitative comparison one should choose definite values of the parameters A, B, α, β.

From the experimental data it can be seen that the gravitational effect in the region $|h_0| > |h_M|$ leads to a decrease in the specific heat of the two-phase system. The same result also follows from formula (3.10) if $3A\beta/B > 1$. Also taking into account the estimate given at the end of section 3 we obtain $2 > 3A\beta/B > 1$. When this inequality is satisfied it follows from formulas (3.9) and (3.10) that the addition to the first term in the specific heat at the critical point (A^2/B in (3.9)) and the differences in the specific heats of the one- and two-phase systems in the "distant" region $|h_0| > |h_\pm|$ (a quantity of the order of $3A^2/2B$ in (3.10)) differ by a factor of 1.5. The same ratio also holds experimentally.

The best agreement between theory and experiment is obtained from the following values of the constants:

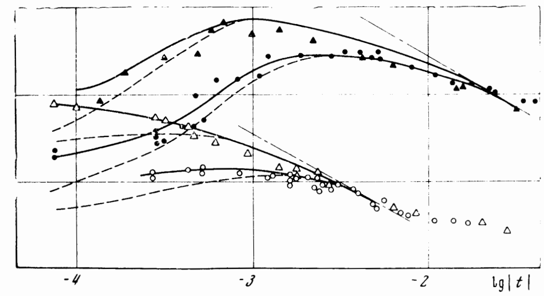

FIG. 2. Comparison of the experimental [2] and the theoretical (sec 3 of the present paper) data on the specific heat in the absence of mixing. The scale is semilogarithmic, i.e., the critical point lies at $-\infty$. Triangles denote the experimental points for a calorimeter of 2.5 cm height, circles denote points for a calorimeter of 8 cm height with black symbols referring to the two-phase system and white symbols referring to a one-phase system. Solid lines are the result of a calculation of the specific heat; dotted lines take into account only the first term in (3.4); the dash-dotted lines give the logarithmic dependence of the specific heat obtained in an experiment with mixing.

$A = 3.8$; $B = 0.6$; $\alpha = 7.5$; $\beta = 5.5 \times 10^{-2}$ (cf., solid curves in Fig. 2). The first three quantities agree completely with those determined previously from independent experiments[5,9], while the value of the constant β turned out to be considerably smaller than that determined by Voronel'[9]. It should be stated that the value $\beta = 0.1-5$ adopted in[8,9] was by no means reliable. Apparently just the experiments being analyzed by us now, and also an investigation of the discontinuity of the specific heat in experiments including mixing, present the most reliable method of determining the constant β.

It appears to us to be useful to study experimentally the motion of the meniscus and to measure the specific heat without mixing of the fluid. Such experiments (for different heights of the vessel and filling densities) could to some extent clarify the problem of the nature of the singularity in the specific heat at the critical point, and also could serve as a means of studying the critical parameters (for example, density in experiments involving a meniscus) and the parameters in the equation of state A, B, α, β and others. We also note that in calorimetric experiments involving mixing such mixing is never ideal, i.e., there will always remain a certain inhomogeneity (in the limit—the correlation radius of density fluctuations). Naturally our formulas are valid also in this case if we interpret h_M as the characteristic dimension of the inhomogeneity (smaller than the height of the vessel). Perhaps it might be possible to obtain this parameter from comparison with experiment, i.e., to judge in this manner the extent of mixing.

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[3)] We call attention to the fact that taking into account only the first term in (3.4) (dotted curve in Fig. 2 for $t > 0$) leads to a systematic deviation from experiment while the remaining terms in (3.4) obviously improve the agreement.

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