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CONTRIBUTION TO THE THEORY OF THE CRITICAL POINT

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An expression for the free energy near the critical point, which agrees with the experimental data [2,3], is proposed. In this case the singularity at the critical point has a logarithmic nature, and a finite nonanlytical term appears.

1. It is well known that the critical point is a singular point on the state curve. A clarification of the character of the singularity of the thermodynamic potentials at this point, and consequently also the singularity of any thermodynamic quantity, is in the realm of microscopic theory, which has not yet been developed. The existing phenomenological theory [1] of the critical point (as well as the theory of second-order phase transitions) essentially starts from an a priori assumption concerning the character of the singularity at this point. Namely, it is assumed that in the main approximation which interests us the thermodynamic potentials behave like smooth functions (i.e., the singularity contains terms of higher order than those retained in the calculation) and the singularity which will be possessed at the critical point by some quantity is then ascertained. This makes it particularly important to check experimentally the deduction of the theory.

C_V and ΔC_V of Ar and O_2 in the immediate vicinity of the critical point were measured at the Thermodynamics Laboratory of VNIIFTRI (Institute for Physico-technical and Radio Measurements). The measurements have shown that the temperature dependence of the specific heat C_V at critical volume has a logarithmic singularity. This contradicts the ordinary theory, according to which C_V remains finite.

It is natural to attempt to construct a theory analogous to the existing one (taking, however, experimental results as the initial assumptions), to ascertain the consequence to which such a theory leads, and to compare just these results with the data obtained in further experiments.

2. The following statements can be regarded as reliably established [$v = (V - V_{cr})/V_{cr}$, $t = (T - T_{cr})/T_{cr}$]:

I. $C_v \big|_{v=0} \sim \partial^2 F/\partial t^2 \sim \ln|t|$;

II. $(\partial p/\partial V)_{T_{cr}} = (\partial^2 p/\partial V^2)_{T_{cr}} = 0$;

III. The quantities

$$F,\ \frac{\partial F}{\partial t} \sim E,\ \frac{\partial F}{\partial V} \sim p,\ \frac{\partial^2 F}{\partial V^2} \sim \frac{\partial p}{\partial V},$$

$$\frac{\partial^2 F}{\partial V \partial t} \sim \frac{\partial p}{\partial t},\ \frac{\partial^3 F}{\partial V^3} \sim \frac{\partial^2 p}{\partial v^2}$$

are finite in the vicinity of the critical point.

IV. The jump in the specific heat ΔC_V on going through the coexistence curve remains finite and not equal to zero at the critical point. According to Krichevskiĭ and Khazanova [4],

$$\Delta C_v = \left\{ \left[\left(\frac{\partial E'}{\partial v'} \right)_T - \frac{E'' - E'}{v'' - v'} \right] \frac{dv}{dt} \right\}_{\text{coex}}, \tag{1}$$

where the prime and the double prime pertain respectively to $v' > 0$ and $v'' < 0$; F is the free energy, E the internal energy, and p the pressure.

3. As an addition to the free energy, satisfying condition I, we choose [1)]

$$F_1 = \psi(t, v) \ln \varphi(t, v) + \chi(t, v); \tag{2}$$

$$(\partial^2 \psi/\partial t^2)_{cr} = \alpha \sim 1,$$

$$\varphi(t, 0) = t^2, \qquad \varphi(t, v) \geqslant 0; \tag{3}$$

$\varphi = 0$ only when $t = v = 0$.

Conditions I—IV, of course, do not suffice to clarify the form of the functions φ and ψ. It therefore becomes necessary to make an additional assumption, which is the main one in the present

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[1)] All quantities will henceforth be written in dimensionless form. The units chosen are the corresponding combinations of the critical parameters.

work, that $\varphi(t, v)$ and $\psi(t, v)$ are regular functions of t and v, while χ and those among its derivatives which will be needed later on are finite (for more details regarding χ see Sec. 4).

By the same token we postulate the form of the singularity of the critical point (agreeing with the available experiments).

From (2)—(3) and conditions II—IV we obtain after simple manipulations

$$F = F_{\text{reg}} + \varkappa_1 t^2 \ln \{(t + \beta v^2)^2 + \gamma^2 v^4\} + \chi(t, v), \quad (4)$$

and the terms omitted in front of and under the logarithm sign are of the order of $v^5 + tv^3$.

4. Let us clarify the character and the role of the function $\chi(t, v)$. The specific heat C_V calculated from (1) and (4) contains in addition to a logarithmic term, even when $\chi \equiv 0$, also a term which is a function of t/v^2, i.e., an addition not defined at the critical point, the value of which depends on the manner with which the critical point is approached. The physical non-uniqueness of the state of the critical point apparently disappears if account is taken of the inhomogeneity of matter near the critical point, connected with the infinite compressibility at this point (see [1]). Such closeness to $t = v = 0$ can hardly be realized experimentally.

Mathematically such a singularity is quite natural. Since the specific heat is not an analytic function when $t = v = 0$ ($C_V \to \infty$ i.e., arbitrarily different values of C_V are realized at arbitrarily close distances to $t = v = 0$), the dependence of the limiting value of a function of two variables on the path on which they approach the limiting point is legitimate.

Thus, a logarithmic singularity leads to a non-uniqueness of the state at the critical point. It is therefore natural to assume beforehand that C_V contains an addition to the term with the logarithmic singularity also a finite addition (which is not unique when $t = v = 0$), dependent on t/v^2. Since $C_V \sim \delta^2 F/\delta t^2$ the function F should contain in addition to a regular part[2] also a term $t^2 h(t/v^2)$ which must follow from the presence of the term $h_1(t/v^2)$ in C_V.

By assumption, the term $t^2 h(t/v^2)$ leads to a finite addition to C_V (the entire part tending to infinity is described, according to (4), by the logarithmic term), i.e.,

$$2h(x) + 4xh'(x) + x^2 h''(x) \sim 1 \quad (x = t/v^2)$$

for arbitrary x. Assuming that $x \to 0$ the limit of the left half is s_0, and that as $x \to \infty$ it is equal to t_0, we get

$$h(x) \sim \begin{cases} \gamma_1/x + \gamma_2/x^2 + s_0 + s_1 x + \cdots, & x \ll 1 \\ \delta_1/x + \delta_2/x^2 + t_0 + t_1/x^3 + \cdots, & x \gg 1 \end{cases}$$

(we note that for arbitrary $x \sim 1$ the function $h(x)$ and its derivatives are finite by assumption). The first two terms, multiplied by t^2, are contained in the regular part of F, and we can therefore expect $h(x)$ to be expandable in powers of x when $x \ll 1$: $h(x) = h_0 + h_1 x + \ldots$ and in powers of $1/x$ when $x \gg 1$: $h(x) = t_0 + \delta_1/x + \ldots$

The term $h(x)$ enters into the smooth part of the thermodynamic quantities so that it is quite difficult to investigate it experimentally. The structure of this term is such that it does not influence the character of the calculated quantities.

The final expressions for the free energy and of the specific heat are

$$F = F_{\text{reg}} + \alpha_1 t^2 \ln[(t + \beta v^2)^2 + \gamma^2 v^4] + t^2 h(t/v^2), \quad (5)$$

$$C_v = C_{v\,\text{reg}} + 2\alpha_1 \ln[(t + \beta v^2)^2 + \gamma^2 v^4] + h(t/v^2). \quad (6)$$

We note that (5) makes it possible to write down the equation of the coexistence curve in coordinates t and v in a very simple form. This curve is in the first approximation a second-degree parabola[3]: $t = -sv^2$, $s = \text{const}$. Consequently, the appearance of the parameter t/v^2 in the free energy is not accidental. This parameter remains constant on the coexistence curve.

It is curious that, as in the existing theory of the critical point [1], the order of the smallest nonvanishing derivative of the pressure with respect to the volume at the critical point $(\partial^3 p/\partial v^3)_{T_{cr}} \neq 0$ determines uniquely the form of the phase equilibrium curve near the critical point: $t \sim v^2$.

5. Some check on formula (5) can be made by plotting the specific heat as a function of the volume with $t = \text{const}$, particularly $t = 0$, using the isochores $C_V = f(t)$ corresponding to different densities of matter. The existing experimental data are not sufficient to construct the complete dependence $C_V(v)$. There are enough data, however, to be able to estimate by how many times

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[2] In the regular part, in contrast with [1], it is necessary to retain the term tv^3, since this is the term responsible for ΔC_V.

[3] The assumption that $dt/dv = 0$ and $d^2t/dv^2 \neq 0$ on the coexistence curve (it is physically obvious that the equation $t = t(v) < 0$ has two roots), which was made in place of statement IV, leads to the same form (5) for the free energy.

the power of v in (6) exceeds that of t. This number turns to be larger than 1.5, and since, in accordance with the conditions indicated above, the function $\varphi(t, v)$ is assumed to be analytic and essentially positive, we might think that formula (5) describes correctly the experimental data. An estimate of the constants β and γ^2 shows that both quantities are of the order of 0.1 in dimensionless units.

The presence of a singularity at the critical point greatly influences the character of thermodynamic quantities. Thus, $(\partial^2 p/\partial t^2)_V \sim (\partial C_V/\partial v)_T$ becomes infinite at the critical point, and does not vanish as indicated for example in the book by Rowlinson [5]. The adiabatic velocity of sound $(\partial p/\partial \rho)_S^{1/2}$, to the contrary, should vanish logarithmically.

An analysis of other consequences of the presence of a singularity at the critical point will be presented in the future.

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