

SPECIFIC HEAT OF WATER NEAR THE MELTING POINT AND ORNSTEIN-ZERNIKE FLUCTUATION CORRECTIONS

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In connection with the problem of investigating the "singularity track" near the crystallization temperature of a liquid [1], the specific heat of water was measured on approaching the crystallization point and in the supercooled state.

The measurements could be extended to -7.5°C . The specific heat of the water continued to increase (Fig. 1). The error in the measurement of the specific heat in the adiabatic calorimeter in this temperature interval, and with such a relatively quiescent object was $\leq 0.1\%$ [2]. This makes it possible to consider the analytic dependence of the specific heat on the temperature, in spite of the fact that this quantity varies by only $\sim 2\%$ in the entire measurement interval.

Recognizing that the temperature T_0 to which the proposed singularity should be related [1] lies considerably below the melting temperature, we should expect the measurement interval to correspond to relatively large values of $t_0 = (T - T_0)/T_0$. In this case we can hope to observe a region of applicability of the self-consistent field approximation with the Ornstein-Zernike fluctuation corrections [3]. Indeed, Fig. 2 shows that the measurement results are compatible with a square-root singularity of the specific heat as a function of the temperature. The presence of such a region does not contradict the idea of the possible existence of a real singularity near T_0 with a "scaling" index (see [1]). Thus, the dependence of the specific heat C_v of water, as well as of other substances, at a critical density in the vicinity of the critical point, has apparently a scaling-type singularity:

$$\frac{C_v}{T} = A t^{-\alpha} + B, \quad (1)$$

where $\alpha \approx 0.13$ and $t = (T - T_c)/T_c$. Nonetheless, at values of t that are relatively large but less than unity, there is a section that agrees well with the root singularity and corresponds to the self-consistent field approximation. Figure 3 reveals such a compatibility of the experimental data with the different asymptotic laws at $t \rightarrow 0$ (formula (1)) and $t \sim 1$:

$$C_v = A^* t^{-0.5} + B^*, \quad (2)$$

The experimental data on the specific heat C_v of water at critical density were taken by us from [4].

The parameter that determines, according to Vaks, Larkin, and Pikin [3], the applicability of the self-consistent-field approximation is the ratio $(a/r_0)^3 = v_m/r_0^3$, where

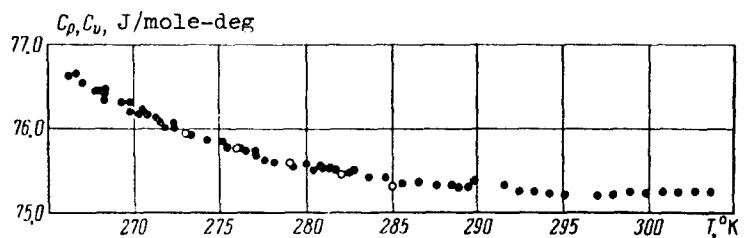


Fig. 1. Temperature dependence of the specific heat of water: \bullet - C_p , \circ - C_v .

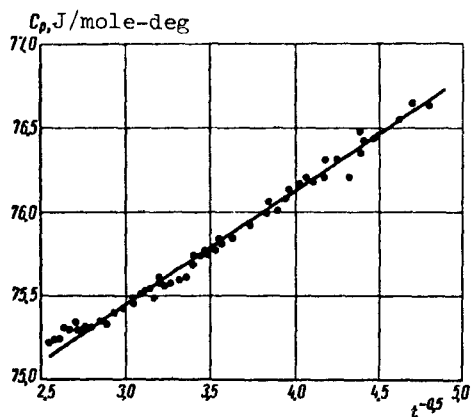


Fig. 2

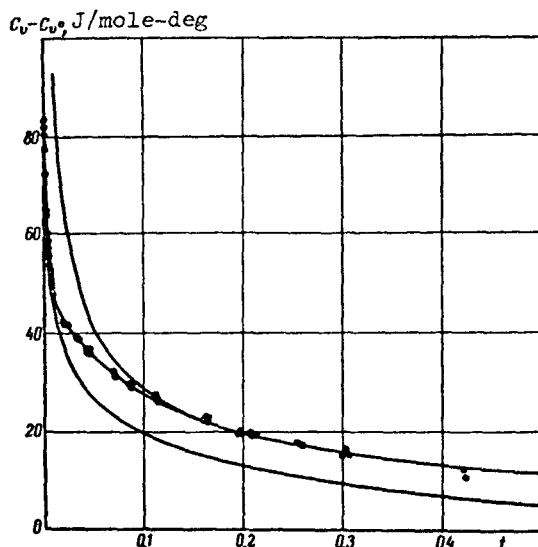


Fig. 3

Fig. 2. Dependence of the specific heat C_p of water on $t^{-0.5}$, where $t = (T - T_0)/T_0$ and $T_0 = 255^\circ\text{K}$.

Fig. 3. Dependence of the specific heat C_v of water at the density $\rho = \rho_c \approx 0.315 \text{ g/cm}^3$. The upper and lower continuous curves correspond to $t^{-0.5}$ and $t^{-0.13}$, respectively, where $t = (T - T_c)/T_c$, and $T_c = 647.31^\circ\text{K}$.

r_0 is the radius of the paired interaction potential and v_m is the volume per molecule of matter. This ratio, for the liquid-vapor critical points, is always close to unity, meaning, generally speaking, that there is no wide interval of applicability of the corresponding approximation. However, in a very narrow region adjacent to $t \leq 1$, such applicability is possible for numerical reasons. This is apparently what we observe for water in Fig. 3 in the region $t > 0.15$.

Indeed, for a cubic Ising lattice [3] we have

$$A^* = \frac{6^{3/2} v_m}{16\pi r_0^3} \quad (3)$$

At $v_m/r_0^3 \sim 1$, to estimate the interval of t in which the Ornstein-Zernike approximation is valid, an important role is played both by the model-dependent numerical coefficient at v_m/r_0^3 , which is connected with the model (see (3)), and by the magnitude of the regular part. For the investigated real systems, these quantities can differ by a factor of several times from those given in [3]¹⁾.

The values of r_0 for oxygen and nitrogen, calculated by us from experimental data of the type shown in Fig. 3, on the basis of the assumption that

¹⁾We note that the quantity r_0 determined from the experiments on light scattering ($r_c = r_0 t^{-\nu}$, where r_c is the correlation radius of the density fluctuations and $\nu \approx 2/3$), is determined accurate to $\sqrt{6}$. The usually employed quantity is smaller by a factor $\sqrt{6}$ than our r_0 .

formula (3) is applicable, turned out to be perfectly realistic ($r_0 = 4.8 \text{ \AA}$ for oxygen and 5.2 \AA for nitrogen), while the parameter v_m/r_0^3 of Vaks, Larkin, and Pikin was almost exactly equal to unity for both substances. For water, such a value of r_0 is 3 \AA . This figure is less meaningful for water than for oxygen and nitrogen, owing to the more complicated molecular structure of the water. The section with the root dependence on Fig. 3 is so narrow that it might be better to speak not of a real approximation but simply of a common tangent. However, if such a common tangent does take place even at critical density, then it is all the more justified to expect a square-root asymptotic form of the type [2] near the crystallization, where the specific volume of the liquid, and consequently, also the parameter of Vaks, Larkin, and Pikin, is smaller by several times.

Since the difference between C_p and C_v for water near room temperatures is negligible ($dv/dT = 0$ at $T = 4^\circ\text{C}$), we assume that our use of the measured values of C_p (see Fig. 1) is justified. It is seen from Fig. 2 that the square-root dependence of the specific heat relative to the temperature $T_0 = 255^\circ\text{K}$ represents our data quite well in the region $t_0 > 0.05$. Thus, the region of applicability of the self-consistent-field approximation shifts towards lower t with increasing density, as expected. The value of r_0 determined from formulas (2) and (3) for crystallizing water turned out to be $r_0 = 4.7 \text{ \AA}$, which is 1.5 times larger than r_0 at the critical point. Since it is difficult to expect the effective radius of the forces for pair interactions to increase near the melting point, the growth of r_0 may signify that it is necessary to take into account unpaired interaction for the crystallization of a liquid.

What is important in the present paper are not so much the numerical values as the fundamental possibility of extracting, on the basis of the Ornstein-Zernike approximation, a microscopic parameter from experimental data on the thermodynamic properties. The applicability of the Ornstein-Zernike approximation offers an attractive possibility of constructing a theory of crystallization on the basis of the self-consistent field.

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OPTICAL ELECTRON-NUCLEAR RESONANCE IN SEMICONDUCTORS

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A considerable number of investigations have by now been made on optical pumping of spin-oriented electrons in semiconductors. The optical-pumping method makes it possible to produce easily a high polarization of the electron spins in the conduction band, and to detect it optically [1 - 3]. The use of this method for the investigation of semiconductors turned out to be very