NOTE ON KIANG'S FORMULA FOR THE CRITICAL EXPONENT δ IN WATER

J. STRAUB

Institute A für Thermodynamik, Technische Hochschule, Munich, Germany

Kiang's formula predicts δ near 6 in H_2O whereas experiments give a δ around 4.2.

Kiang [1] recently proposed a formula relating the critical exponent δ defined by $P - P_c \sim$ $\sim (\rho - \rho_c)^\delta$ at $T = T_c$ to the compressibility factor $P_c/\rho_c k_B T_c$:

$$P_c/\rho_c k_B T_c = \zeta(2 + 1/\delta)/\zeta(1 + 1/\delta) \qquad (1)$$

where P is the pressure, ρ the particle density and ζ the zeta-function. Eq. (1) follows from the droplet model for the liquid gas transition [2], if its formulas are applied also to droplets with few molecules only. ($\zeta(x) = \sum_l l^{-x}$, where l here counts the number of molecules within the liquid droplet.) A priori one should therefore not expect eq. (1) to be valid because the droplet model assumptions are made for large droplets only [2]. But this relation is in good agreement with experimental results for some simple liquids (CO_2, Xe, H_2, He) and is accurate [1] within 5 to 10% in the Van der Waals gas and for some lattices of the three-dimensional and the two-dimensional Ising model (δ = 3, 5.2, and 15, respectively). If the critical behavior of quantities like $\rho - \rho_c$ or the curvature of the vapor pressure curve $d^2 P_{vap}/dT^2$ is calculated from the droplet model then only large droplets enter the results; but in [3] also $(\rho - \rho_c)/\rho_c$ at T_c and $(T_c^2/P_c)d^2 P_{vap}/dT^2$ were calculated; thus the 'dangerous' zeta-functions enter also in some

numerical factors, and these were found [3] to agree approximately with experiment [4]. Thus as long as no better theory exists the accuracy of eq. (1) can be checked by experiment only. For H_2O it predicts [1] δ = 6.2.

We present in fig. 1 H_2O isotherms at T_c from [5] together with corresponding data [6, 7] for CO_2. They show δ = 4.2 in H_2O in a region which is for CO_2 sufficiently near the critical point to fix δ. According to [8] β = 0.35 for H_2O ($0.2 \leq \rho - \rho_c \leq 0.7$; $\rho_{gas} - \rho_{liquid} \sim (T_c - T)^\beta$ at the coexistence curve). Thus the critical isotherm in fig. 1 seems not to be measured in a transition region between a Van der Waals region ($\beta = \frac{1}{2}$, δ = 3) and the critical region. In addition scaling laws predict [8] δ = 4.4 in H_2O.

We conclude that δ in H_2O is nearer to the values usually observed in other phase transitions than to the higher values predicted by eq. (1) for polar gases. A possible explanation might be the long range dipole forces in H_2O. If the droplet model assumptions are extrapolated to very small droplets this approximation can be worse in H_2O than in other gases with a shorter molecular interaction range.
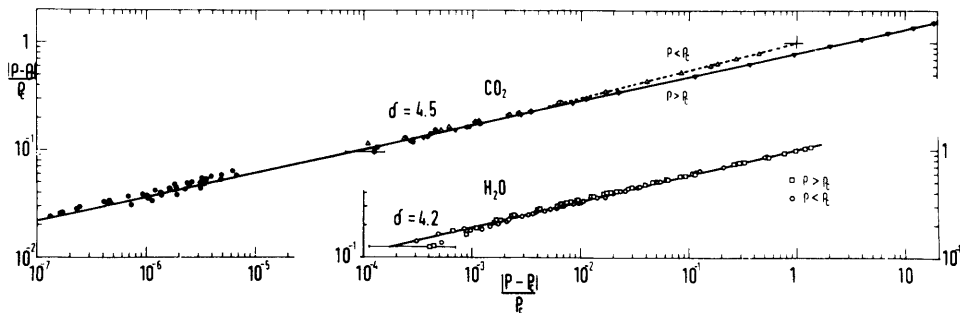
Fig. 1. Critical isotherm of H_2O [5] and CO_2 [6, 7]. The H_2O values are shifted by a factor 10 in $\rho - \rho_c/\rho_c$.

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