

Observation of Singular Diameters in the Coexistence Curves of Metals

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We report the first reliable determination of the liquid-vapor coexistence curves of the metals cesium and rubidium. Both curves are noticeably different from those of nonmetallic fluids in their extreme vapor-liquid asymmetry which causes the law of rectilinear diameter to break down. The functional form of the diameter is consistent with the suggestion by Goldstein and Ashcroft that the strong state dependence of the effective interparticle forces leads to large amplitudes of the $1 - \alpha$ anomaly.

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A great deal of effort has been devoted to the study of fluid metals in the liquid-vapor critical region. Much of this effort concerned the metal-nonmetal transition which occurs in the liquid when it is made to expand by heating to critical conditions.¹ For the alkali metals Cs and Rb specifically, recent measurements of the electrical conductivity² and the static susceptibility³ as well as nuclear magnetic resonance experiments⁴ have indicated that there exists a link between the liquid-vapor and the metal-nonmetal transition. On the other hand, the information concerning the character of the critical point itself is still sketchy and does not include direct information on the exact location of the critical point or the role played by the metal-nonmetal transition. The occurrence of the latter implies that the nature of the interparticle interaction must change dramatically, from metallic to a van der Waals-type interaction. Such a change would be expected to influence considerably the properties of fluid metals in the critical region.⁵

In this Letter we report the first experimental results which clearly demonstrate that the liquid-vapor coexistence curves of metals are noticeably different from those of nonmetallic fluids. The two branches of the coexistence curve are strongly asymmetric and we find that the law of rectilinear diameter breaks down over a large temperature range. As far as we know, such a large amplitude for the diameter anomaly has never before been observed in any one-component fluid.

Because of the severe experimental problems connected with the high critical temperatures of metals, we used a conventional technique of pVT measurement to determine the coexistence-curve data of Cs and Rb. Carefully measured isochores were intersected with the vapor-pressure curve, yielding T, ρ points on the coexistence curve. The high-temperature, high-pressure sample environments necessary for these measurements were achieved within an internally heated steel pressure vessel. A cylindrical molybdenum cell contained the samples, and the cell pressure was automatically balanced against that of the surrounding argon gas by means of an external connecting capillary with negligible volume. The cell was surrounded by an electric furnace which was thermally in-

sulated from the walls of the pressure vessel. The furnace consisted of three independently controlled molybdenum heating elements. The sample temperature was measured with five calibrated W-Re thermocouples in close contact with the cell. From numerous measurements of the vapor pressure with different amounts of liquid metal in the cell, we found that the reproducibility of the temperature measurement $\Delta T/T$ was better than $\pm 10^{-3}$ and that the temperature gradients ΔT within the cell were about $\Delta T/T_A \approx 10^{-3}$, where T_A is the average temperature. The maximum relative error of the density determination was smaller than $\pm 1\%$. All quantities were measured relative to the critical data, for which $T_c = 1924$ K, $p_c = 92.5$ bars, and $\rho_c = 0.379$ g/cm³ for Cs and $T_c = 2017$ K, $p_c = 124.5$ bars, and $\rho_c = 0.292$ g/cm³ for Rb have been found. These new data, especially T_c , deviate strongly from the old values in the literature,⁶⁻⁹ which have been determined partly with rules obeyed by nonmetallic fluids. Whether such rules are valid for metals is, however, one of the points at issue.

Our results for the intercepts of the isochores and the vapor-pressure curve are summarized in Table I. A reliable determination of the intercepts is not possible closer than 2°C from the critical point. In this region, the isochores become almost confluent with the vapor-pressure curve.

Figures 1(a) and 1(b) show plots of the coexisting liquid (ρ_L) and vapor (ρ_V) phases of cesium and rubidium and of their diameters versus temperature. Both coexistence curves are remarkably different from those of nonmetallic fluids in their extremely asymmetric shapes and strong curvature of the diameters over a surprisingly large temperature range. In contrast, the diameters for nearly all simple nonmetallic one-component fluids are found to be linear over large temperature ranges. Thus far a deviation from a linear diameter has been reported only for a relatively small temperature range close to the critical point of SF₆.^{13,14} However, there are strong theoretical arguments, based on model systems¹⁵⁻¹⁸ and renormalization-group studies,¹⁹⁻²¹ in favor of the existence of a singular diameter for all fluids, all suggesting that the temperature derivative of the diameter $\rho_d = (\rho_L + \rho_V)/2\rho_c$

TABLE I. Experimental values for the liquid (ρ_L) and vapor (ρ_V) densities at the liquid-vapor coexistence curves of Rb and Cs.

Rubidium				Cesium			
T (°C)	ρ_L (g/cm ³)	T (°C)	ρ_V (g/cm ³)	T (°C)	ρ_L (g/cm ³)	T (°C)	ρ_V (g/cm ³)
1391	0.801	1190	0.015	1452	0.871	1393	0.074
1410	0.792	1295	0.025	1477	0.838	1395	0.074
1411	0.789	1357	0.032	1503	0.807	1460	0.091
1469	0.743	1400	0.039	1533	0.767	1487	0.096
1482	0.739	1482	0.056	1550	0.743	1525	0.114
1482	0.738	1518	0.06	1569	0.713	1537	0.119
1544	0.686	1613	0.091	1585	0.685	1563	0.134
1573	0.659	1670	0.116	1597	0.658	1580	0.145
1598	0.635	1700	0.138	1607	0.625	1590	0.154
1599	0.637	1722	0.17	1622	0.596	1602	0.164
1646	0.58	1725	0.171	1627	0.569	1612	0.173
1647	0.583	1731.5	0.189	1638	0.539	1632	0.219
1676	0.535	1741	0.232	1643	0.509	1639	0.242
1682	0.533	1738	0.252	1650	0.440	1645	0.279
1707	0.482	1743-1744	0.272	1650-1651	0.429	1648	0.302
1714	0.467	1743-1744	0.28	1650-1651	0.404	1649	0.312
1728	0.428			1650-1651	0.382	1650	0.326
1729.5	0.428					1650-1651	0.358
1736	0.381					1650-1651	0.335
1738.5	0.353						
1742	0.331						
1743-1744	0.321						
1743-1744	0.294						

diverges at least as fast as the constant-volume specific heat C_V , that is, that $\rho_d - 1$ behaves as $|\tau|^{1-\alpha}$, where α is the same exponent that governs the behavior of C_V and $\tau = (T_c - T)/T_c$.

The experimental detection of this effect is complicated by the fact that the $|\tau|^{1-\alpha}$ term may be masked by the presence of other terms with similar magnitudes and similar exponents.²² Firstly, it has been shown²³ that if one particular function, e.g. ρ , has a $|\tau|^{1-\alpha}$ singularity, then any less-symmetric function ρ' , where ρ' is an analytic function of ρ (e.g., $\rho = v^{-1}$), behaves as $|\tau|^{2\beta}$, where β is the exponent which describes the shape of the coexistence curve near T_c . Thus the sought-for effect will be missed unless the correct function is chosen. There are strong but not conclusive arguments for supposing that ρ is the appropriate function.²⁴ Secondly, studies of different fluid properties have revealed that corrections to asymptotic scaling must be applied when the range accessible to experimentation exceeds the range of asymptotic validity of the scaling laws.^{25,26} For instance, the expansions for the coexisting densities have the form^{19,21,24}

$$\frac{\Delta\rho}{\rho_c} = \frac{\rho_L - \rho_V}{2\rho_c} = B_0|\tau|^\beta + B_1|\tau|^{\beta+\Delta_1} + \dots, \quad (1)$$

$$\rho_d = \frac{\rho_L + \rho_V}{2\rho_c} = 1 + D_0|\tau|^{1-\alpha} + D_1|\tau| + D_2|\tau|^{1-\alpha+\Delta_1}. \quad (2)$$

On the other hand, Goldstein and Ashcroft⁵ have suggested that the strong curvature of the diameter for metals is caused by a dominant contribution of the leading term in Eq. (2). Therefore we shall first analyze the singular asymptotic behavior of the diameters for Rb and Cs by the use of a single power law. We do this in order to guard against the possibilities that we may bias our experimental results by imposing on them an existing theoretical construct.

In Figs. 2(a) and 2(b) we plot $\log(\Delta\rho/\rho_c)$ and $\log(\rho_d - 1)$ vs $\log|\tau|$. Fitting with the leading terms in Eqs. (1) and (2) we find $B_0 = 2.25$, $\beta = 0.355 \pm 0.01$, $D_0 = 2.1$, and $1 - \alpha = 0.87 \pm 0.03$ for Cs; and $B_0 = 2.45$, $\beta = 0.360 \pm 0.01$, $D_0 = 2.3$, and $1 - \alpha = 0.86 \pm 0.03$ for Rb. A single power law applies over a range $10^{-3} < |\tau| < 10^{-1}$ and the apparent experimentally determined $1 - \alpha$ values are very close to the theoretical value 0.89. It must be pointed out, however, that it is difficult to deduce an exact exponent value from our data. Because of the severe experimental problems connected with the high critical temperatures of metals, reliable experimental data can only be obtained for $|\tau| \geq 10^{-3}$ which is probably near the outer limit of the asymptotic scaling range in fluids. According to Eqs. (1) and (2), many terms, each with an adjustable amplitude, are needed then to describe the behavior of the coexistence curve and the coexistence-curve diameter. We have attempted to fit Eqs. (1) and (2) to our

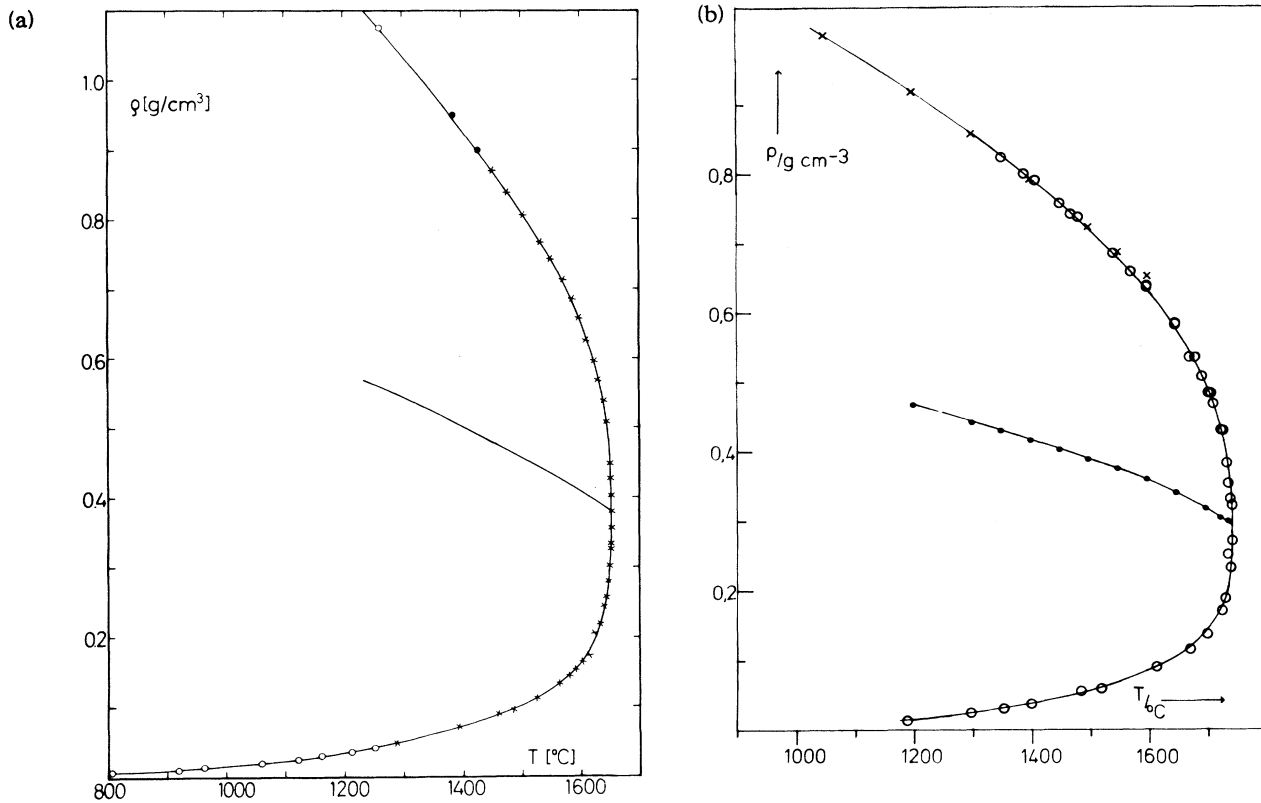


FIG. 1. (a) Liquid-vapor coexistence curve of Cs. Crosses, present work; filled circles, Franz (Ref. 10); open circles, Stone *et al.* (Ref. 11). (b) Liquid-vapor coexistence curve of Rb. Open circles, present work; crosses, Pfeifer (Ref. 12).

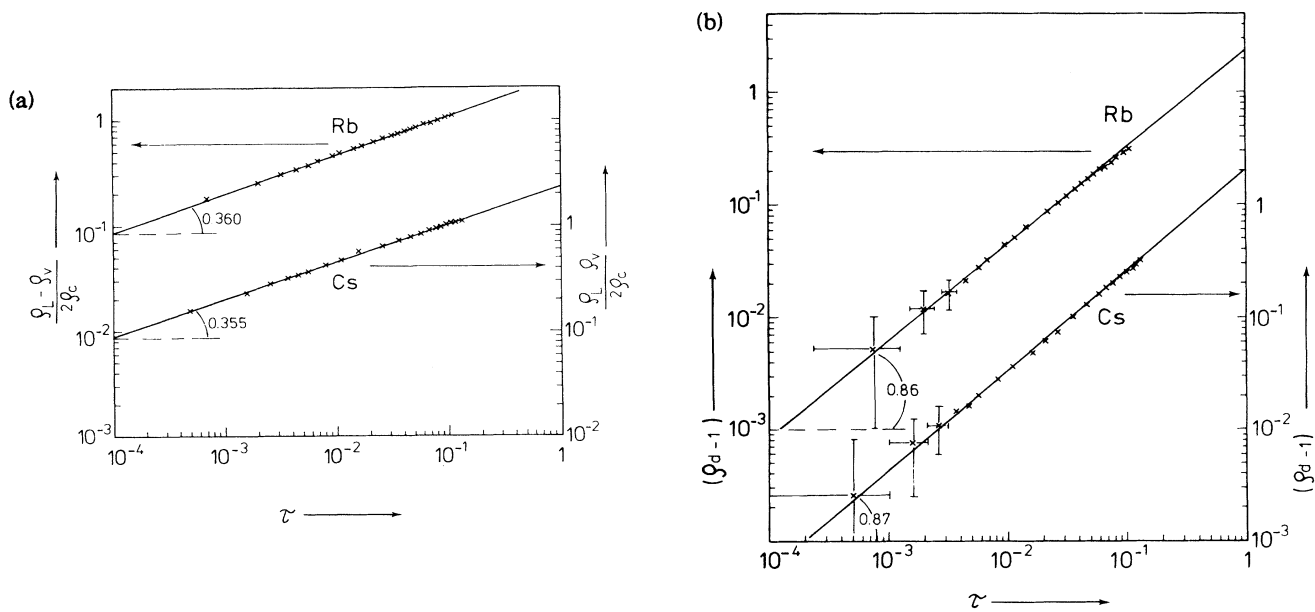


FIG. 2. (a) Single-power-law analysis of the coexisting liquid and vapor densities of Cs and Rb. (b) Single-power-law analysis of the diameter singularities for Cs and Rb.

data using the theoretically predicted exponent values $1 - \alpha = 0.89$, $\beta = 0.327$, and $\Delta_1 = 0.5$. A least-squares program with B_0 , B_1 , D_0 , D_1 , and D_2 as adjustable parameters gives excellent fits with a mean standard deviation of the experimental points from the fitted curves of less than 0.1%. However, it must be pointed out that this procedure is insufficient to rule out the 2β anomaly. In order to test for the presence of the 2β anomaly, we fitted Eq. (3) to the diameter for rubidium (for which the data are most abundant) in terms of both density, $\rho' = \rho$, and volume, $\rho' = v$, over $10^{-3} < |\tau| \leq 10^{-1}$:

$$\rho'_d = 1 + A_1|\tau| + A_2|\tau|^{1-\alpha} + A_3|\tau|^{2\beta}. \quad (3)$$

For the density ρ the amplitude of the 2β term is about 30 times smaller than the amplitude of the $1 - \alpha$ term, whereas for the volume v both amplitudes become comparable. This is consistent with the assumption that ρ is the appropriate function for the order parameter.²⁴

In conclusion, we have found that the coexistence curves of Cs and Rb are asymmetric compared with those of simple fluids. The asymmetry is very similar to that observed in two other metallic systems, namely, metal-ammonia solutions²⁷ and electron-hole liquids.²⁸ The data strongly support the suggestion⁵ that the strong state dependence of the effective interparticle forces, and especially the changes in such forces in the course of the metal-nonmetal transition, lead to very large amplitudes of the $1 - \alpha$ anomaly in the diameters of the liquid-vapor coexistence curves of metals.

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