SCALING-LAW EQUATION OF STATE FOR GASES IN THE CRITICAL REGION

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(Received 1 May 1967)

The Widom-Kadanoff scaling-law equation of state has been confirmed for a variety of gases in a range of ±50% of the critical density and within a few percent above and below the critical temperature. Using a new procedure motivated by the scaling law, the exponent δ describing the shape of the critical isotherm was found to be close to 5 while the compressibility exponents γ and γ' were both found to be equal to about 1.4.

Scaling law.—Recently Widom,[1] Kadanoff,[2] and Griffiths[3] have put forward ideas about the nature of the equation of state in the critical region. For the magnetic case, Griffiths proposes the following relation between magnetic field H, magnetization M, and temperature T:

$$H(M,t)=|M|^{\delta}\operatorname{sgn}(M)h(x), \tag{1}$$

where $t=(T-T_c)/T_c$ and $x=t/|M|^{1/\beta}$; for the exponents we follow Fisher's[4] notation. In this so-called scaling-law equation of state, $h(x)$ is an analytic function of x in the range $(-x_0,\infty)$, where $x=-x_0$ defines the coexistence curve. The scaling laws imply both the validity of the Rushbrooke-Griffiths inequalities[5,6] as equalities, and the identity of primed and unprimed exponents (below and above T_c); thus only two of the exponents can be chosen independently. Such a scaling-law equation of state exhibits nonclassical critical anomalies with proper choice of $h(x)$ and the exponents β and δ.

So far, tests of the scaling laws have been made only along the special curves[7] critical isochore, critical isotherm, and coexistence curve. An exception is the work of Kouvel and Rodbell[8] who showed that a scaling-law equation of state holds for the ferromagnet CrO_2 at temperatures above T_c. In this Letter we show that a scaling-law equation of state is also valid in the critical region of gases above and below T_c. With the insights thereby gained we propose a new way of deriving critical exponents from experimental data.

We had the option to translate the H-vs-M language into a pressure-volume[9] or into a chemical potential–density[10] language. We have chosen the latter because, as Tisza and others[3,10] have pointed out, it is much more symmetric around the critical isochore. The scaling-law equation of state then becomes

$$\Delta\mu(\rho,T)=|\Delta\rho|^{\delta}\operatorname{sgn}(\Delta\rho)h(x), \tag{2}$$

where μ = chemical potential, ρ = density, $\Delta\rho=(\rho-\rho_c)/\rho_c$, $\Delta\mu=[\mu(\rho,t)-\mu(\rho_c,t)]\rho_c/P_c$, and $x=t/|\Delta\rho|^{1/\beta}$.

The data which we will try to scale are PVT data obtained by classical methods for CO_2,[11] Xe,[12] SF_6,[13] and Ar,[14] as well as density versus height isotherms for CO_2,[15,16] N_2O,[15] and $CClF_3$,[15] from recent optical experiments on gravity-produced density gradients.

The PVT data were transformed to $\mu\rho T$ data by graphical-numerical integration. The optical data did not require transformation since reduced height and chemical potential are simply related by $\Delta\mu=-\Delta h$.

We have been rigorous in rejecting all classical PVT data for which gravity effects were appreciable. The criterion used was that $P(\rho,t)-P(\rho_c,t)$ should be at least three times larger than the hydrostatic head in the cell. Furthermore we have rejected data which were inconsistent within the general body of related data. This leads to the exclusion of the CO_2 data and some of the SF_6 data of Ref. 13, as well as several of the optical curves.

For $T>T_c$, μ-vs-ρ isotherms seem to have a center of symmetry on the critical isochore. The published optical data[15,16] sometimes show an apparent shift of this center of symmetry. Since the absolute density for these data is, for a variety of reasons, less well known than the relative density difference, we adjusted the zero of the density scale in each figure so as to coincide with the symmetry center of the isotherms.

Our test of the scaling laws was carried out using a transformation of Eq. (2),

$$\frac{|\Delta\mu(\rho,t)|}{|t|^{\beta\delta}}=\frac{h(x)}{|x|^{\beta\delta}}=G\frac{|\Delta\rho|}{|t|^{\beta}} \tag{3}$$

so that the scaled chemical potential $z=|\Delta\mu(\rho,t)|/|t|^{\beta\delta}$ is a universal function of the scaled density $y=|\Delta\rho|/|t|^{\beta}=|x|^{-\beta}$. The function $G(y)$

consists of two branches, one for $t > 0$ and one for $t < 0$, which join asymptotically for $y \to \infty$ (critical isotherm).

We have scaled data for $\Delta\mu$ and $\Delta\rho$ for which t was sufficiently larger than the relative error in T_c; for β and δ we choose 0.35 and 5, respectively, for reasons given below.

The result of the scaling is given in Fig. 1. Data covering a range of ±50% in the density $\Delta\rho$ and from −3 to +10°C (−0.5 to 3%) in temperature all fall nicely on the two branches of the universal curve.

Striking features of the curves are the following: z depends linearly on y in the range $y < 0.4$, i.e., for data close to the critical isochore away from the critical temperature; low- and high-temperature branches coalesce for $y > 4$, i.e., for data close to the critical isotherm away from the critical density; the two branches after coalescence follow an approximate 5th-power behavior; for small y and t negative, that is close to the coexistence curve, a constant value $y = 1.9$ is approached.

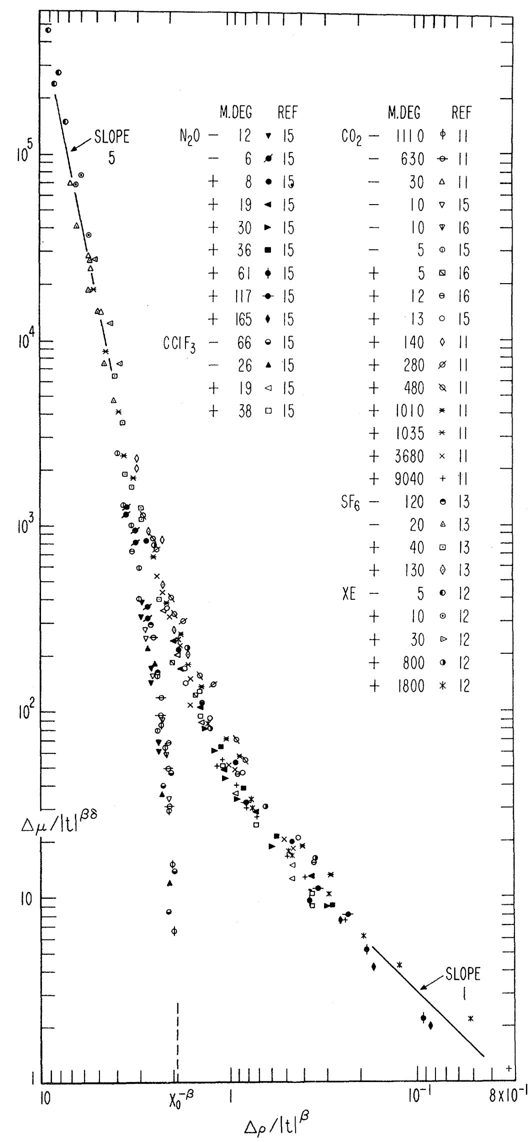

FIG. 1. Scaled chemical potential $|\Delta\mu|/|t|^{\beta\delta}$ versus scaled density $|\Delta\rho|/|t|^{\beta}$ in the critical region of several gases, using $\beta = 0.35$ and $\delta = 5$.

It should be remarked here that those xenon data of Ref. 12 which are simultaneously within 40 mdeg and within 15% in density of the critical point are out of line with the universal curve of Fig. 1. We therefore took the option of rejecting these data rather than the general body of all other PVT data, classical as well as optical. The only explanation which we can give for the discrepancy is that these are the data which would be most severely affected by stirring. For similar reasons, we have accepted the SF_6 data of Ref. 13 rather than those of Ref. 12, where stirring took place.

Exponents.—We have made an independent analysis of the critical isotherm in order to justify the value 5 used in the test of the scaling laws. Since values of ρ in the neighborhood of 4.2 have been obtained[9] by analyzing some of the same data as we have used, we will explain our method of analysis in some detail. There are two coupled difficulties which must be overcome in the analysis of the critical isotherm. First of all, the experimental temperature will always be somewhat above or below the critical temperature. Thus every experimental isotherm must deviate from the critical isotherm if the density comes close enough to the critical density. Secondly, for classical PVT measurements gravity effects vitiate all data close to the critical point.

We have circumvented the first difficulty by analyzing not only the behavior of the isotherm closest to critical but also parts of all isotherms in the critical region. Without making any commitment to the precise values of the exponents used, Fig. 1 can be interpreted to mean that every isotherm in the critical region approaches the critical isotherm for large enough values of $\Delta\rho$. Thus parts of all isotherms in the critical region can be used to determine δ, namely those segments for which

$$|\Delta\rho|/|t|^{\beta} > 4. \tag{4}$$

Since parts of isotherms as much as 1°K from

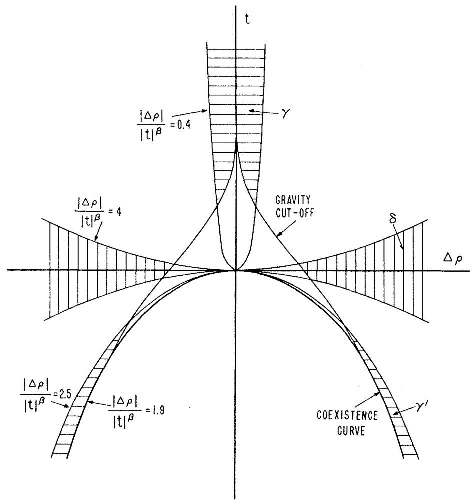

FIG. 2. Reduced temperature-density plane showing the critical region of gases, with critical isochore, critical isotherm, and coexistence curve. The shaded areas indicate regions in which data were used for determination of γ, δ, and γ' respectively. Data within the gravity cut-off curve, the location of which depends on the particular experiment, have not been used.

the critical satisfy this criterion, they were included in the analysis.

The wealth of data allowed by (4) enabled us to be rigorous in excluding data affected by gravity, according to the criterion mentioned above. This eliminates the second difficulty encountered in this type of analysis.

All data acceptable under the two criteria fall in the shaded region indicated in Fig. 2. In Fig. 3, $\Delta\mu$ is plotted for these data as a function of $\Delta\rho$ on a logarithmic scale. We see that the appropriate portions of all isotherms lie on a single straight line which can be identified with the critical isotherm. Over a range of five orders of magnitude in $\Delta\mu$ this line can be represented by

$$|\Delta\mu| = \Delta\,|\Delta\rho|^{\delta}. \tag{5}$$

If a linear least-squares fit of $\log\Delta\mu$ vs $\log\Delta\rho$ is made in accordance with (5), then we find $\delta = 5.06$ with standard deviation 0.06 based on 78 points (the data of Ref. 16 were not used in the fit). For Δ we find 0.76 ± 0.05. If the classical PVT data alone are fitted, then $\delta = 4.73$ with standard deviation 0.10 based on 43 points, and $\Delta = 0.56 \pm 0.07$.

The data seem to exclude values of δ around 4.2 previously reported whereas 5 is well within the acceptable range.

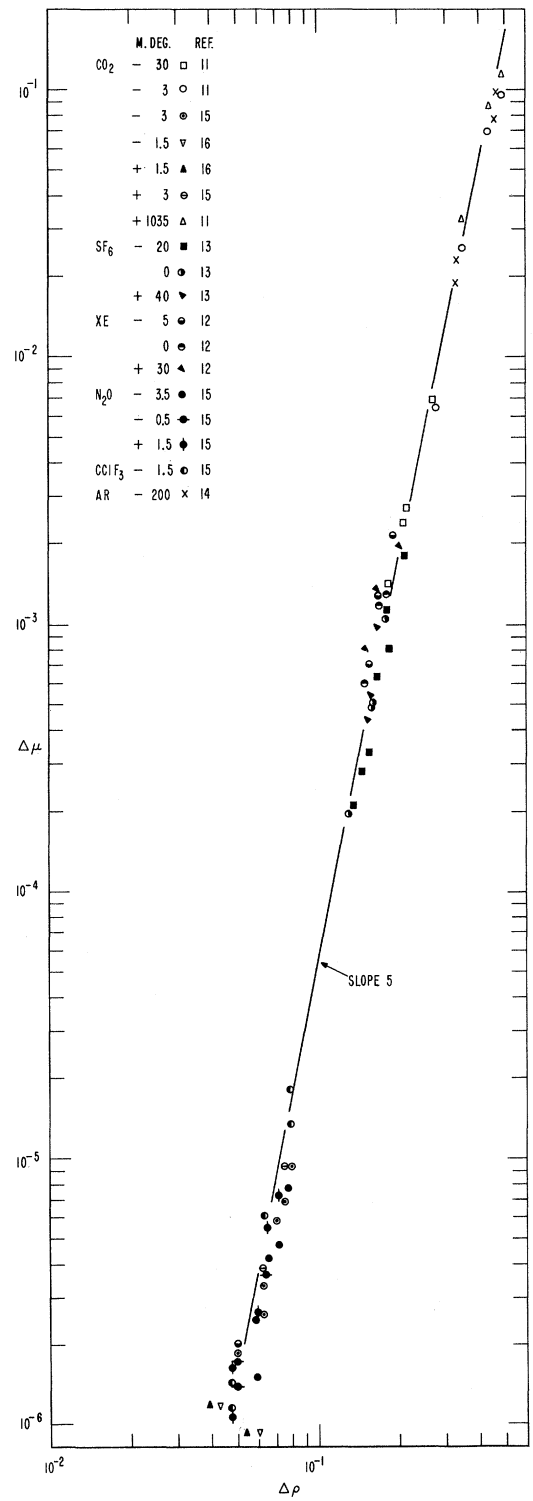

FIG. 3. Reduced chemical potential $\Delta\mu$ versus reduced density $\Delta\rho$ along portions of various isotherms after coalescence with the critical isotherm.

The exponent γ was determined using similar criteria. As indicated in Fig. 1, all supercritical isotherms have a linear portion for $y<0.3$. Taking slopes from this linear region and rejecting all classical PVT data affected by gravity we obtain the lower curve of $(\partial\mu/\partial\rho)_T$ vs t in Fig. 4. Subcritical data were treated in an analogous manner and are shown in the upper curve. Since we are dealing with a derivative the points used for the determination scatter more than those used for δ. The regions in the T-ρ plane where points suitable for this analysis were taken are indicated in Fig. 2. The scaling-law relation $\gamma=\gamma'=\beta(\delta-1)$ and the values chosen for β and δ would imply $\gamma=\gamma'=1.4$. Figure 4 shows that this is not in conflict with the data.

The value of 0.35 chosen for β agrees with values for this parameter obtained by Michels,[11] Lorentzen,[16] and Weinberger and Schneider.[12,6] It should, however, be noted that the value of α implied by the scaling-laws relation $2-\alpha'=\beta(\delta+1)$, $\alpha=\alpha'$, is slightly negative. We regard this as a discrepancy which needs further explanation, possibly by small changes in β and δ.

Conclusion.—We have shown that the scaling laws successfully describe the PVT behavior of a variety of gases in a large region around the critical point. Using a method motivated by, but independent of, the scaling laws, we have found δ to be circa 5 in a range of five decades in $\Delta\mu$, unequivocally different from the values around 4.2 previously obtained. We have re-evaluated γ and γ' and found them to be equal and somewhat larger than previously reported. We have also found that the optical measurements and the classical PVT data are in substantial agreement.

We could not have analyzed the optical data properly without the generous cooperation of Dr. J. Straub, Technische Hochschule, München, in all stages of the work. During the course of the investigation we had several fruitful discussions with Dr. M. E. Fisher.

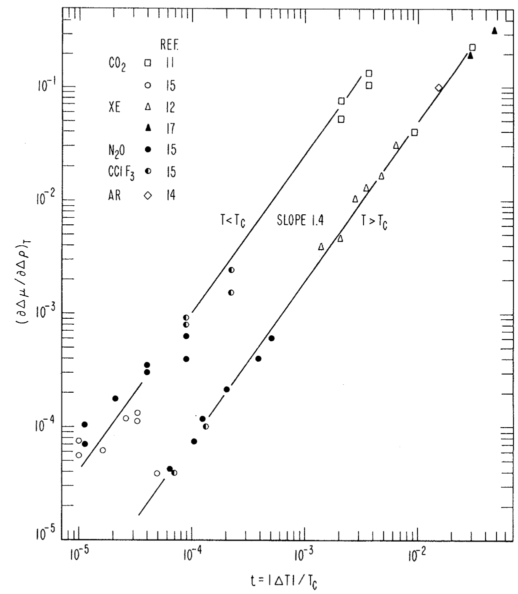

FIG. 4. $\partial\Delta\mu/\partial\Delta\rho$ versus reduced temperature $|t|$ along the critical isochore for $t>0$ and along the coexistence curve for $t<0$.

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SCATTERING OF MICROWAVES FROM PLASMA SPACE-CHARGE WAVES NEAR THE HARMONICS OF THE ELECTRON GYROFREQUENCY*

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(Received 17 May 1967)

An instability near the harmonics of the electron gyrofrequency has been observed by the method of combination scattering. The instability has been stimulated by a strong external microwave signal propagating along the magnetic field near the cyclotron resonance.

The analysis of plasma fluctuations and radiations near the electron-cyclotron harmonics has been undertaken by many investigators.[1] An observation of plasma waves using the method of combination[2] scattering of a weak microwave signal permits the effects which cause the fluctuation to be clearly separated from the method of detection. Using this approach, we have observed a plasma instability near the harmonics of the electron gyrofrequency which is stimulated by the presence of another, strong, microwave signal.

The experiment was performed in a very low-pressure argon gas ionized by an electron beam [Fig. 1(a)]. The plasma interacts with an external microwave field in a coaxial cylinder which is below cutoff in the circular waveguide section for all frequencies involved with the exception of frequencies very close (~100 Mc/sec) to the electron-cyclotron frequency (ω_c). The average plasma density was obtained by measuring the onset frequency of radiation coupling from the circular waveguide section to the dipole antenna as the frequency approached the cyclotron resonance.[3] The plasma profile and relative density changes were observed by a small movable double Langmuir probe. A sweep generator provided a microwave signal having frequency $\omega_x \sim \omega_c \sim 2\pi \times 3$ Gc/sec; a fraction $\sim 10^{-3}$ of this was modulated at 7 kc/sec and then coupled with the unmodulated part at the coaxial waveguide. The power level ($\lesssim 100$ mW) of the unmodulated portion could be separately controlled relative to the modulated signal. A radiometer detected the signal converted by the plasma to a frequency $\omega_r = \omega_x + \omega$ (ω = space charge wave frequency, $\omega_r = 2\pi \times 9.2$ Gc/sec) which is reflected from the below-cutoff circular waveguide section; the radiometer was phase locked to the modulated part of the incident signal. To obtain the spectrum of the electrostatic waves, ω_x was swept slowly over a given range near the cyclotron frequency in order to enhance the microwave interaction with the plasma.[4] In this manner the demodulated signal provided by the radiometer is insensitive to the plasma thermal radiation and is affected by the unmodulated part of the incident wave only to the extent that

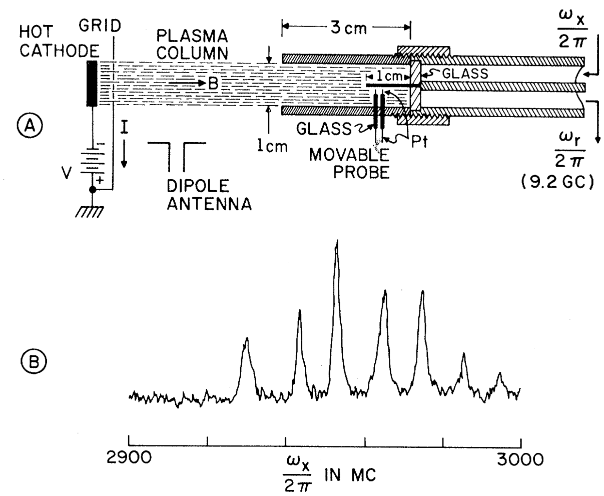

FIG. 1. (a) The apparatus. Gas pressure 5×10^{-4} Torr, argon; $V \sim 100$ V, $I \sim 50$ mA. (b) Typical scattering resonances observed at 9.2 Gc/sec when the transmitter signal is swept. Magnetic field is $\omega_c/2\pi = 3.12$ Gc/sec; space-charge wave frequencies are $>2\omega_x'$, $\omega_x = \omega_x'$.