THERMODYNAMIC ANOMALIES OF CO_2, Xe, AND He^4 IN THE CRITICAL REGION

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A closed-form equation for the chemical potential as function of density and temperature, based on the scaling idea, is fitted to experimental data in the critical regions of CO_2, Xe, and He^4, optimizing δ, T_c, and two adjustable constants. Values obtained for the critical exponents and the two constants vary only slightly from substance to substance; we find $\beta = 0.35\text{-}0.36$, $\delta = 4.4\text{-}4.6$, implying $\gamma \sim 1.25$, $\alpha \sim 0.05$; $\Gamma/\Gamma' = 3.6\text{-}4.4$, $\Delta = 2.6\text{-}3.3$. Agreement with previous estimates and with independent C_v and optical-density-gradient measurements is discussed.

The scaling-law equation of state for the critical region, recently proposed by Widom,[1] Griffiths,[2] and others,[3] is a partial asymptotic formulation of thermodynamic behavior near a critical point, and it incorporates the well-known critical anomalies with equal exponents above and below T_c:

$$\text{coexistence curve, } t<0\text{: } \Delta\rho = B(-t)^{\beta};$$

$$\text{critical isotherm, } t=0\text{: } P(\rho, T_c) - P(\rho_c, T_c) \sim \mu(\rho, T_c) - \mu(\rho_c, T_c) = \Delta(\Delta\rho)|\Delta\rho|^{\delta-1};$$

$$\text{compressibility, on the critical isochore, } t>0\text{: } K_T = \Gamma t^{-\gamma};$$

$$\text{along the coexistence curve in the one-phase region, } t<0\text{: } K_T = \Gamma'(-t)^{-\gamma};$$

$$\text{specific heat at constant volume, on the critical isochore, } t>0\text{: } C_v \simeq (A^{+}/\alpha)[t^{-\alpha}-1];$$

$$\text{on the critical isochore, } t<0\text{: } C_v \simeq (A_{\mathrm{II}}^{-}/\alpha)[(-t)^{-\alpha}-1];$$

$$\text{along the coexistence curve in the one-phase region, } t<0\text{: } C_v \simeq (A_{\mathrm{I}}^{-}/\alpha)[(-t)^{-\alpha}-1];$$

$$\text{jump in } \rho C_v \text{ when crossing phase boundary, } t<0\text{: } \Delta(\rho C_v) = A^{-}(-t)^{-\alpha}. \qquad (1)$$

For fluids, in Griffiths' formulation, using quantities made dimensionless by appropriate combinations of critical parameters, the chemical potential $\Delta\mu = \mu(\rho, t) - \mu(\rho_C, t)$ is an antisymmetric function of $\Delta\rho = (\rho - \rho_c)/\rho_c$ at constant temperature and can be expressed as follows:

$$\Delta\mu = \Delta\rho|\Delta\rho|^{\delta-1}h(x)$$

with

$$x = t/|\Delta\rho|^{1/\beta} \text{ and } t = (T-T_c)/T_c. \qquad (2)$$

$h(x)$ is analytic in its range of definition, $-x_0 < x < \infty$, equals 0 at $x = -x_0$, the coexistence curve, and possesses a series expansion of the type

$$h(x) = \sum_{\eta=1}^{\infty} \eta_n x^{\beta(\delta+1-2n)} \qquad (3)$$

near $x = \infty$, so that μ is analytic in t and $\Delta\rho$ across the critical isochore for all $t > 0$.[2] There are also conditions on derivatives of $h(x)$ in order to fulfill thermodynamic stability conditions. Equation (2) implies validity of the Griffiths-Rushbrooke[4] thermodynamic inequalities between exponents as equalities. The scaling law (2) implies that the quantity $h(x) = \Delta\mu/|\Delta\rho|^{\delta}$ is a function of one variable $x = t/|\Delta\rho|^{1/\beta}$ only or, alternatively, that

$G(y)=\Delta\mu/|t|^{\beta\delta}$ is a function of $y=|\Delta\rho|/t^{\beta}$ only. It is this last formulation that we used in our previous analysis[5] of the scaling properties of fluids; by plotting $G(y)$ vs y for several gases we showed that isotherms in the critical region coincided reasonably well on a single curve. The scatter around the curve was due to several causes. One should expect deviations of corresponding states between the various substances. The choice of parameters T_c, β, and δ was not optimized and it was assumed but not proven that the exponents are the same for all substances. It was not clear whether all experimental points were in the asymptotic range where the scaling law would hold. Finally, the possibility of systematic experimental error in some data cannot be excluded.

In this Letter we summarize the results of a detailed study, to be published elsewhere,[6] of the experimental behavior of fluids in the critical region, in which we paid attention to all these factors. The substances CO_2,[7] Xe,[8] and He^4[9] were analyzed separately in order to detect possible deviations from corresponding states. By choosing a closed form for representing $h(x)$ one could do the scaling as a least-squares problem, optimizing several of the parameters. Also, we investigated the range of validity of the asymptotic Eq. (2). Using the maximum available range of $\Delta\rho$ and t in which $\Delta\mu$ was antisymmetric in $\Delta\rho$, we noted that some points deviated systematically from the fitted equation and that the exponents varied somewhat when the range was changed. The data were assumed to be in the asymptotic range when for further reduction of the ranges of $\Delta\rho$ and t the values of the parameters became steady and systematic deviations were absent.

We propose the following equation for $h(x)$:

$$h(x)=E_1\left(\frac{x+x_0}{x_0}\right)\times\left[1+E_2\left(\frac{x+x_0}{x_0}\right)^{2\beta}\right]^{[\beta(\delta-1)-1]/2\beta}, \qquad (4)$$

where the factor $(x+x_0)/x_0$, suggested by Widom,[1] ensures $h(x)$ to be zero at $x=-x_0$; E_1 and E_2 are adjustable constants.

The expression (4) can be shown to fulfill all criteria formulated by Griffiths except for the form of the series expansion (3) at large x. The first three derivatives of $\Delta\mu$ with respect to $\Delta\rho$, however, are of the right form at $x\to\infty$. Equation (4) predicts the correct behavior for the compressibility along the coexistence curve; higher derivatives are not well behaved at $x=-x_0$. Expression (4) is a form for $h(x)$ with a small number of adjustable parameters, namely x_0, β, δ, E_1, and E_2, and implicitly T_c and ρ_c. It is suitable for a least-squares analysis of experimental data. Writing

$$g(x)=\left[\frac{x_0h(x)}{x+x_0}\right]^{2\beta/(\gamma-1)}, \qquad (5)$$

where $h(x)$ and x now represent the experimental quantities $|\Delta\mu|/|\Delta\rho|^{\delta}$ and $t/|\Delta\rho|^{1/\beta}$, respectively, we have

$$g(x)=E_1^{2\beta/(\gamma-1)}\left[1+E_2\left(\frac{x+x_0}{x_0}\right)^{2\beta}\right]; \qquad (6)$$

therefore $g(x)$ is a linear function of $\{(x+x_0)/x_0\}^{2\beta}$.

We have fitted the properly weighted values of $g(x)$ as a linear function of $\{(x+x_0)/x_0\}^{2\beta}$ by a least-squares fit, thus obtaining estimates for

Table I. Critical parameters for CO_2, Xe, and He^4.

Parameter	CO_2	Xe	He^4
		Fit of coexisting densities	
β	0.350 ± 0.008	0.350 ± 0.008	0.359 ± 0.002
x_0	0.135 ± 0.010	0.186 ± 0.020	0.360 ± 0.005
ρ_c	236.7 amagat	1.08 g/cm^3	0.0691 g/cm^3
T_c	30.94 ± 0.04°C	16.590 ± 0.004°C	5.1889 ± 0.002°K
		Fit of $\Delta\mu,\Delta\rho,t$ data using scaling law	
ρ_c	236.7 amagat	1.110 g/cm^3	0.0693 g/cm^3
T_c	30.96 ± 0.04°C[a]	16.58 ± 0.03°C[a]	5.1884 ± 0.0008°K[a]
δ	4.60 ± 0.06[a]	4.6 ± 0.1[a]	4.45 ± 0.10[a]
E_1	2.36 ± 0.02	2.96 ± 0.07	2.78 ± 0.03
E_2	0.30 ± 0.02	0.37 ± 0.03	0.48 ± 0.03

[a] In most cases the error bars are standard deviations obtained by least-squares analysis. The ones marked, however, have been ascertained by observing that systematic deviations from the fitted equation are present if the parameter is varied by this amount or more.

E_1 and E_2. β, x_0, and ρ_c were not varied but rather taken from an independent fit of coexistence curves to be published separately.[10] We have performed the least-squares analysis for a number of values of T_c and δ and chosen those that give a minimum standard deviation. We found that we could use all data in the range of antisymmetry of $\Delta\mu$, which is about +30% in $\Delta\rho$, except for some points of large $\Delta\rho$ at the highest temperatures, with t around 0.03. The results of our analysis of the data on CO_2, Xe, and He^4 are summarized in Table I. Figure 1 shows the form of the function $\ln h(x)$ vs $\ln[(x+x_0)/x_0]$ for the three substances, and it is indicative of the quality of the scaling.

It should be noted that the representation of the scaling-law equation of state in terms of $h(x)$ is simpler, smoother, and thus more attractive than our previous representation $G(y)$. In particular, there is no break in the functional form of $h(x)$ at $x=0$.

The values of the constants in the definitions of the critical anomalies Eq. (1) are simply related to the constants in our Eq. (4) except for the coefficients of the specific heat which require numerical integration:

$$\Delta = E_1(1+E_2)^{(\gamma-1)/2\beta},$$

$$\Gamma^{-1} = x_0^{-\gamma}E_1(E_2)^{(\gamma-1)/2\beta},$$

$$\Gamma'^{-1} = \beta^{-1}x_0^{-\gamma}E_1,$$

$$\Gamma/\Gamma' = \beta^{-1}E_2^{(1-\gamma)/2\beta},$$

$$\Delta(\rho C_v) = \beta x_0^{\alpha-2}E_1(-t)^{-\alpha}. \tag{7}$$

The values of the critical exponents and coefficients derived from the parameters of Table I are shown in Table II.

It is evident from Fig. 1 that Eq. (4) describes the experimental PVT data for CO_2, Xe, and He^4 within their estimated precision. For He the specific-heat parameters found from (4) agree well with values we derived from directly measured C_v data[11]:

	α	A_{II}^-	A^+	A^-
From C_v	0.06 ± 0.01	1.35 ± 0.42	1	0.4
From Eq. (4)	0.05	1.42	1.06	0.36

We had no difficulty fitting the coexistence curve, the PVT data, and the C_v data all with the same values of the critical parameters.[9] For Xe the agreement between the calculated C_v parameters and those derived from experimental C_v data[12] is less striking. For this substance precise data for the vapor pressure curve P_s are available as well. Fitting these with a scaling-law-based expression we could make a third estimate of the specific-heat anomaly since in the scaling-law picture the anomaly of C_v is the same as that of $(\partial^2P/\partial T^2)_{\rho c}$. The three sets of parameters show agreement in order of magnitude:

	α	A_{II}^-	A^+	A^-
From C_v	0.065	4.4	2.8	⋯
From Eq. (4)	0.04	4.8	3.7	1.2
From P_s	0.04	5.8		
$=a+bt+ct^2+dt^{2-\alpha}$	0.06	5.2		

It should be realized that the experimental C_v values, not at our disposal, were fitted with α slightly different from ours.

The ratio of the compressibility coefficients Γ/Γ' is different from our previous estimate[5] which was obtained by graphical determination of slopes of isotherms. This is difficult to do reliably near the coexistence curve. Our new values of Γ/Γ' and γ agree reasonably well with those of Wilcox and Balzarini who used optical interferometry very near the critical point.[13] This is an indication that asymptotic behavior may set in at fairly large distances from the critical point and can thus be inferred from data not very close to critical.

From Table II it appears that the only parameter varying greatly from substance to substance is x_0. The other parameters β, δ, E_1, and E_2 are remarkably steady. We do not yet have the statistical tools for deciding whether the small dif-

Table II. Critical exponents and coefficients for CO_2, Xe, and He^4.

Parameter	CO_2	Xe	He^4
γ	1.26	1.26	1.24
α	0.04	0.04	0.05
Γ	0.0526	0.059	0.130
Γ'	0.0119	0.0143	0.0359
Γ/Γ'	4.4	4.1	3.62
Δ	2.6	3.3	3.2
A^+	4.24	3.70	1.06
A_{II}^-	5.80	4.80	1.42
A^-	1.56	1.10	0.36

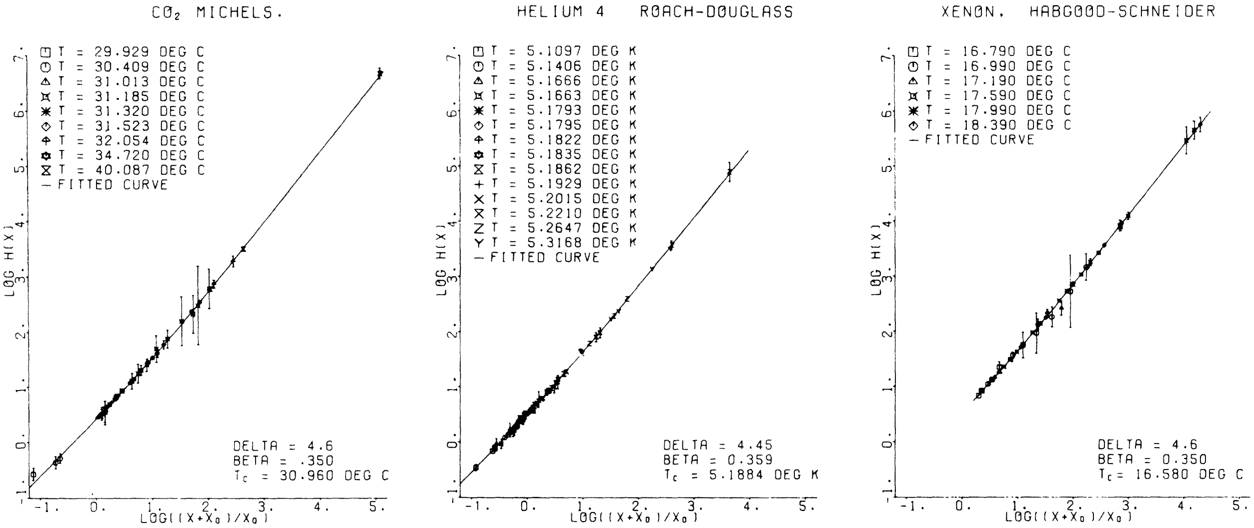

FIG. 1. Agreement between calculated curves and experimental data. The solid lines represent Eq. (4) with optimized parameters from Table I. The error bars on the experimental points reflect realistic estimates of errors in pressure, temperature, and density.

ferences found are significant. If not, the critical isotherms of the three gases should coincide. Our previous study of the critical isotherm,[5] implicitly assuming this correspondence, yielded a value of δ somewhat higher than the ones found here. This must be due to a slight displacement of the optical data used before.[14] Since a very small temperature gradient in the optical data could cause this displacement, we do not necessarily ascribe this offset along the critical isotherm a result of changing behavior very near the critical point.

We have concluded that: (1) The experimental *PVT* data in the critical region of He^4, CO$_2$, and Xe, after transforming to variables $\Delta\mu$, $\Delta\rho$, t, can be scaled (Fig. 1). (2) The proposed form (4) of a scaling-law equation describes the data of the three gases to within their estimated precision (Fig. 1). (3) The range of validity of the scaling law is approximately ±30 % in $\Delta\rho$ and -0.01, $+0.03$ in t. (4) The behavior of C_v derived from this equation agrees fairly well with directly measured C_v data for Xe and excellently with similar data for He^4. (5) The values of the critical exponents vary only slightly from substance to substance. There is hardly if any dependence on the quantum parameter Λ^*.[15] (6) The coefficients E_1, E_2 in our equation do not vary appreciably from substance to substance. (7) The deviations from corresponding states in the critical region are therefore almost completely described by the parameter x_0, or B alone, which parameter varies considerably from substance to substance.

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EIGENVALUES OF THE LIOUVILLE EQUATION FOR A ONE-DIMENSIONAL SYSTEM

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We investigate the nonequilibrium properties of N distinguishable, classical, point particles on a ring of length L, in the limit $N, L \to \infty$ and $N/L \to d$; the dynamics consists of a velocity-dependent probability of penetration. In particular, we identify the eigenvectors of the Liouville equation and find the corresponding eigenvalues, the real portions of which are the negative inverse relaxation times.

We first consider N classical point particles of equal mass constrained, like beads, to a ring of circumference L. Further, the particles are distinguishable, labeled by the integers $1, 2, \cdots, N$; otherwise our problem would become the trivial one of free particles. We shall be interested in nonequilibrium properties when $N, L \to \infty$ and $N/L \to d$. The dynamics is the following: When two particles, say 1 and 2, collide with relative velocity $v_{12} = |v_1 - v_2|$, we allow them to penetrate with probability $p(v_{12})$:

$$p_{12} = \frac{|v_{12}|}{c + |v_{12}|}, \quad c \geqslant 0. \tag{1}$$

The reason for choosing this particular function of v_{12} instead of a more general one will become clear when we discuss the solution.

We note that p_{12} vanishes for small relative velocities and approaches 1 for large relative velocities. Further, p_{12} contains a parameter c which can be varied from free particles, $c = 0$, to hard rods,[1,2] $c \to \infty$. We might then call our problem that of "soft" rods.

Thus, the model we are considering is a true many-body problem. It contains a stochastic element from the beginning, and hence is not time-reversal invariant; it cannot be derived from a Hamiltonian.

In this note, we investigate the eigenfunctions of the Liouville equation

$$\partial\Psi/\partial t = L\Psi = \alpha\Psi, \tag{2}$$

where

$$\Psi = \exp(\alpha t)\psi(z_1, z_2, \cdots, z_N).$$

z_j is both the velocity and position coordinate for the jth particle. It is clear that collisions in this problem merely rearrange velocities without changing their values. Thus if we start with velocities $v_1 < v_2 < \cdots < v_N$, these particular values are conserved by the Liouville operator L. We shall assume that the velocities are in fact distributed with a density $\rho(v)$, normalized so that $\int \rho(v) dv = d$.

Consider a particular arrangement of particles and velocities on the ring, first without regard for identities. The particles are ordered with coordinates $0 \leqslant x_1 < x_2 < \cdots < x_N < L$, the set of which is denoted by X. The first particle has a label $Q1$ and velocity $P1$, the second $Q2$ and $P2$, etc. $Q1, Q2, \cdots$ and $P1, P2, \cdots$ are two permutations of the integers $1, 2, \cdots, N$ denoted by Q and P. Therefore, we may designate a state of the system by (X, Q, P), and an eigenfunction ψ is a function of (X, Q, P).

We assume that ψ is given by Bethe's hypothesis in the following form: Given a set of complex numbers $k_1, k_2, \cdots, k_N$, whose real and imaginary parts increase with the index, then

$$\psi(X, Q, P) = A(Q, P) \exp(i \textstyle\sum_j x_j k_{Pj}). \tag{3}$$

The Liouville operator, when no $x_j = x_{j+1}$, is

$$L = -\textstyle\sum_j v_{Pj} (\partial/\partial x_j); \tag{4}$$

thus the eigenvalues α are given by

$$\alpha = -i \textstyle\sum_j v_j k_j. \tag{5}$$

We must then show that the boundary conditions