Gravity effects in fluids near the gas–liquid critical point

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The presence of a gravitational field leads to both practical and fundamental limits of the resolution in critical phenomena experiments in fluids near the gas-liquid critical point. We present equations that yield estimates of the gravitational limitations in a variety of critical phenomena experiments for a large number of fluids and as a function of the magnitude of the gravitational field. Various strategies for improving the resolution of such experiments are discussed, including procedures that remove a fluid from thermodynamic equilibrium (e.g., stirring). A comparison is made between the gravitational limitations in earth-bound experiments and those at the micrograviational levels that may become accessible in an orbiting laboratory.

CONTENTS

I. INTRODUCTION

Near the gas-liquid critical point, gravity induces a density gradient in the fluid (Gouy, 1892; Teichner, 1904; Baehr, 1954). The resulting inhomogeneous distribution of the local properties of the fluid strongly affects the interpretation of critical phenomena experiments in fluids (Weinberger and Schneider, 1952). A number of investigators have studied the consequences of gravitationally induced inhomogeneities for the interpretation of critical phenomena experiments such as specific heat measurements (Chashkin *et al.*, 1967; Berestov *et al.*, 1969, 1973; Berestov and Malyshenko, 1970; Schmidt, 1971; Hohenberg and Barmatz, 1972; Lipa *et al.*, 1977) and light-scattering measurements (Alekhin *et al.*, 1969; Chalyi and Alekhin, 1971; Dobbs and Schmidt, 1973; Spittorf and Miller, 1974; Kim *et al.*, 1974; Lakoza *et al.*, 1974; Leung and Miller, 1975, 1977a and b; Sysoev and Chalyi, 1976; Cannell 1977b).

A particularly detailed and quantitative evaluation of gravity effects near the gas-liquid critical point was made by Hohenberg and Barmatz (1972). Our further study of gravity effects was motivated by the following considerations. According to the principle of critical-point universality, fluids near the gas-liquid critical point belong to the universality class of three-dimensional Ising-like systems, i.e., systems with short-range forces and a one-component order parameter (Kadanoff, 1971, 1976). Attempts to verify the validity of this principle have revealed (Hocken and Moldover, 1976; Levelt Sengers *et al.*, 1977) that truly asymptotic critical behavior is not reached unless one approaches the critical temperature to within 0.01%. Therefore, while modern experimental techniques enable one to probe this critical region with substantial accuracy, an accurate assessment of the limits imposed by gravity has become increasingly important. Furthermore, in the near future the opportunity will become available to perform critical phenomena experiments in a space laboratory (Dodge *et al.*, 1975; Moldover *et al.*, 1976; Morrell, 1977; Sengers and Moldover, 1978a). It thus has become desirable to analyze gravity effects as a function of the level of the gravitational field, so as to compare the gravity-induced limitations in earth-bound experiments with those at the microgravitational levels that may become accessible in an orbiting laboratory. It is the purpose of this paper to present methods for estimating the magnitude of these effects in a variety of critical phenomena experiments and for a large number of fluids.

Near the consolute point of binary liquid mixtures the gravitational field leads to the formation of concentration gradients (Yvon, 1937; Voronel and Giterman, 1965; Lorentzen and Hansen, 1966; Blagoi *et al.*, 1970; Mistura, 1971; Fannin and Knobler, 1974; Greer *et al.*, 1975; Giglio and Vendramini, 1975; Maisano *et al.*, 1976a and b; Kwon *et al.*, 1977). However, the relaxation time needed for these concentration gradients to obtain their equilibrium value is excessively large (Greer *et al.*, 1975). In practice one tries to avoid gravity effects by performing the measurements over a time scale small compared to the formation of the gradients. Nevertheless, in many cases gradients may develop during the experiments, but it is difficult to attain true thermodynamic equilibrium (Block *et al.*, 1977; Giglio and Vendramini, 1978; Knobler and Scott, 1978). Because of these complications we focus our attention here on experiments near the gas-liquid critical point of one-component fluids.

We shall proceed as follows. In Sec. II we present critical region parameters that characterize the asymptotic behavior of thermodynamic properties and the correlation length of many fluids near the gas–liquid critical point. For this purpose we assume the validity of the hypothesis of critical-point universality and describe the thermodynamic properties in terms of parametric equations. In Sec. III we summarize the parametric equations for the height dependence of local fluid properties in the presence of a gravitational field.

The inhomogeneities induced by the gravitational field lead to both practical and fundamental limitations in the interpretation of critical phenomena experiments in fluids. The practical limitations are due to averaging errors, since all experimental probes sample the fluid over a finite height. These limitations depend on the magnitude of the gravitational field, the height of the sample volume, and the quantity being averaged. In Sec. IV we estimate the gravitationally induced averaging errors in measuring density, compressibility, and specific heat. In Sec. V we discuss the practical limitations imposed by gravity in some optical experiments. In the case of light-scattering experiments, we also compare these limitations with limitations due to multiple scattering and attenuation of the light. These estimates pertain to experiments in which the fluid is in a state of thermodynamic equilibrium in which the density gradients are fully developed. In Sec. VI we make some comments on attempts to suppress the establishment of density gradients by bringing the system into a suitable nonequilibrium state.

The fundamental or intrinsic limits imposed by gravity are due to the fact that, sufficiently close to the critical point, the fluid properties begin to vary significantly over heights that are of the order of the correlation length. Under these circumstances the local properties of the fluid in a gravitational field can no longer be identified with those of a hypothetical homogeneous system in the thermodynamic limit. These effects are discussed in Sec. VII. A summary of some of our conclusions is presented in Sec. VIII.

II. CRITICAL REGION PARAMETERS FOR FLUIDS

Let T be the absolute temperature, P the pressure, V the volume, ρ the mass density, F the Helmholtz free energy, S the entropy, μ the chemical potential per unit mass, $\chi_T = (\partial\rho/\partial\mu)_T$ a symmetrized isothermal compressibility, and C_v the heat capacity at constant volume. The thermodynamic properties are made dimensionless by expressing them in units of appropriate combinations of the critical temperature T_c, the critical density ρ_c, and the critical pressure P_c

$$T^* = \frac{T}{T_c}, \rho^* = \frac{\rho}{\rho_c}, P^* = \frac{P}{P_c}, F^* = \frac{F}{P_c V}$$
$$\mu^* = \frac{\mu\rho_c}{P_c}, \chi_T^* = \frac{\chi_T P_c}{\rho_c^2}, S^* = \frac{ST_c}{P_c V}, C_v^* = \frac{C_v T_c}{P_c V}. \tag{2.1}$$

Note that the reduced extensive thermodynamic properties F^*, S^*, and C_v^* are taken per unit volume (Sengers and Levelt Sengers, 1978). We also introduce the differences

$$\Delta T^* = \frac{T - T_c}{T_c}, \Delta\rho^* = \frac{\rho - \rho_c}{\rho_c}, \Delta\mu^* = \frac{\{\mu(\rho, T) - \mu(\rho_c, T)\}\rho_c}{P_c}. \tag{2.2}$$

The singular behavior of various properties near the critical point is characterized by power laws. In particular, the specific heat at the critical density above and below T_c diverges as $C_v^*/T^* = (A/\alpha)|\Delta T^*|^{-\alpha}$ and $C_v^*/T^* = (A'/\alpha)|\Delta T^*|^{-\alpha}$, the compressibility in the one-phase region above and below T_c diverges as $\chi_T^* = \Gamma|\Delta T^*|^{-\gamma}$ and $\chi_T^* = \Gamma'|\Delta T^*|^{-\gamma}$, the difference between liquid and vapor densities at coexistence varies as $\Delta\rho^* = B|\Delta T^*|^{\beta}$, and the chemical potential along the critical isotherm varies as $\Delta\mu^* = D\Delta\rho^*|\Delta\rho^*|^{\delta-1}$. The correlation length in the one-phase region above and below T_c diverges as $\xi = \xi_0|\Delta T^*|^{-\nu}$ and $\xi = \xi_0'|\Delta T^*|^{-\nu}$. The critical exponents satisfy the exponent relations $2 - \alpha = \beta(\delta + 1)$, $\gamma = \beta(\delta - 1)$ and $\gamma = (2 - \eta)\nu$, where the exponent η characterizes the asymptotic behavior of the correlation function at the critical point. We also assume the validity of the hyperscaling relation $d\nu = 2 - \alpha$, where $d = 3$ is the dimensionality (Fisher, 1967, 1974).

According to the universality hypothesis (Kadanoff, 1971, 1976; Hubbard and Schofield, 1972), the critical exponents and scaling functions describing fluid properties near the critical point should be the same as those for Ising-like spin systems. For the purpose of this paper we have adopted the exponent values

$$\alpha = 0.11, \beta = 0.325, \gamma = 1.24,$$
$$\delta = 4.815, \nu = 0.63, \eta = 0.03 \tag{2.3}$$

as calculated most recently by Le Guillou and Zinn-Justin (1977) and by Baker *et al.* (1978) for this universality class. There exist small discrepancies between these exponent values and those obtained from series expansion estimates for the three-dimensional Ising model (Camp *et al.*, 1976; Baker, 1977). Our choice is based on the observation that the interpretation of currently available fluid data seems more consistent with the exponent values obtained via the renormalization group approach (Chang *et al.*, 1976; Ley-Koo and Green, 1977).

Explicit expressions for a scaled thermodynamic potential and a scaled equation of state that incorporate the power laws in a thermodynamically consistent way, are obtained by introducing parametric variables (Josephson, 1969). Various parametric equations have been proposed in the literature (Schofield, 1969; Ho and Lister, 1970; Wilcox and Estler, 1971; Kierstead, 1973; Tarko and Fisher, 1975). Here we use the "re-

TABLE I. Restricted cubic model equations.[a]

	$\left(b^2=\frac{3}{3-2\beta},\ c=\frac{2\beta\delta-3}{3-2\beta}\right)$
Variables	$\Delta T^*=r(1-b^2\theta^2)$
	$\Delta\rho^*=r^{\beta}k\theta(1+c\theta^2)$
Chemical potential	$\mu^*=\mu^*(\rho_c^*,T^*)+r^{\beta\delta}a\theta(1-\theta^2)$
Compressibility	$\chi_T^*=(\partial\rho^*/\partial\mu^*)_T=r^{-\gamma}\frac{k}{a}$
	$(\partial\chi_T^*/\partial\rho^*)_T=-r^{-\beta\delta}2\gamma b^2\theta/aq(\theta)$
Helmholtz free energy	$F^*=F_0^*(T^*)+\rho^*\mu^*(\rho_c^*,T^*)+r^{2-\alpha}akf(\theta)$
Pressure	$P^*=-F_0^*(T^*)+r^{\beta\delta}a\theta(1-\theta^2)+r^{2-\alpha}ak\{\theta^2(1-\theta^2)(1+c\theta^2)-f(\theta)\}$
Entropy	$S^*=-\frac{dF_0^*(T^*)}{dT^*}-\rho^*\frac{d\mu^*(\rho_c^*,T^*)}{dT^*}+r^{1-\alpha}aks(\theta)$
Pressure coefficient	$\left(\frac{\partial P^*}{\partial T^*}\right)_\rho=-\frac{dF_0^*(T^*)}{dT^*}+r^{1-\alpha}aks(\theta)+(1+\Delta\rho^*)r^{\beta\delta-1}a\beta\theta\{\delta(1-\theta^2)(1+3c\theta^2)-(1-3\theta^2)(1+c\theta^2)\}/q(\theta)$
Heat capacity	$\frac{C_V^*}{T^*}=-\frac{d^2F_0^*(T^*)}{dT^{*2}}-\rho^*\frac{d^2\mu^*(\rho_c^*,T^*)}{dT^{*2}}+r^{-\alpha}ak\{(1-\alpha)(1+3c\theta^2)s(\theta)-\beta(1+c\theta^2)\theta s'(\theta)\}/q(\theta)$
Correlation length	$\xi=r^{-\nu}\xi_0R(\theta)$
	$(\partial\xi/\partial\rho^*)_T=-r^{-(\nu+\beta)}\xi_0\{2\nu b^2\theta R(\theta)-(1-b^2\theta^2)R'(\theta)\}/kq(\theta)$
Auxiliary functions[b]	
(1)	$f(\theta)=f_0+f_2\theta^2+f_4\theta^4+f_6\theta^6\simeq-0.770+2.359\theta^2-1.660\theta^4-0.059\theta^6$
where	$f_0=-\frac{\beta(\delta-3)-b^2\alpha\gamma}{2b^4(2-\alpha)(1-\alpha)\alpha}+\frac{c\{b^2(1+\alpha)(3\gamma+2\beta)-6\gamma\}}{2b^6(2-\alpha)(1-\alpha)\alpha(1+\alpha)}$
	$f_2=+\frac{\beta(\delta-3)-b^2\alpha(1-2\beta)}{2b^2(1-\alpha)\alpha}-\frac{c\{b^2(1+\alpha)(3\gamma+2\beta)-6\gamma\}}{2b^4(1-\alpha)\alpha(1+\alpha)}$
	$f_4=-\frac{1-2\beta}{2\alpha}+\frac{c\{b^2(1+\alpha)(3-2\beta)-3\gamma\}}{2b^2\alpha(1+\alpha)}$
	$f_6=-\frac{(3-2\beta)}{2(1+\alpha)}c$
(2)	$s(\theta)=s_0+s_2\theta^2+s_4\theta^4\simeq1.456-2.274\theta^2-0.073\theta^4,\ s'(\theta)=2s_2\theta+4s_4\theta^3$
where	$s_0=-(2-\alpha)f_0,\ s_2=-(2-\alpha)b^2(1-2\beta)f_0-\gamma f_2,\ s_4=-3\gamma c/2b^2(1+\alpha)$
(3)	$q(\theta)=2\beta\delta b^2\theta^2(1-\theta^2)+(1-3\theta^2)(1-b^2\theta^2)\simeq1-0.281\theta^2-0.166\theta^4$
(4)	$R(\theta)=1+0.16\theta^2,\ R'(\theta)=0.32\theta$
Amplitudes	$B=k(1+c)/(b^2-1)^{\beta}\simeq1.602k$
	$D=a(b^2-1)b^{3(\delta-1)}/k^{\delta}(b^2+c)^{\delta}\simeq0.281a/k^{\delta}$
	$\Gamma=k/a$
	$\Gamma'=(b^2-1)^{\gamma}k/a\simeq0.203k/a$
	$A=-ak(2-\alpha)(1-\alpha)\alpha f_0\simeq0.143ak$
	$A'=-ak(2-\alpha)(1-\alpha)\alpha(f_0+f_2+f_4+f_6)/(b^2-1)^{2-\alpha}\simeq0.278ak$

[a] Note: $-F_0^*(T^*)=P^*(\rho_c^*,T^*)$ and $\mu^*(\rho_c^*,T^*)$ are analytic functions of temperature that represent, respectively, the pressure and chemical potential along the critical isochore $\rho^*=\rho_c^*=1$.

[b] The numerical estimates correspond to $\beta=0.325$ and $\gamma=1.240$.

stricted cubic model" defined by the equations (Ho and Lister, 1970)

$$\Delta T^*=r(1-b^2\theta^2),$$
$$\Delta\rho^*=r^{\beta}k\theta(1+c\theta^2), \tag{2.4}$$
$$\Delta\mu^*=r^{\beta\delta}a\theta(1-\theta^2),$$

in terms of two auxiliary or parametric variables r and θ. In this representation k and a are two system-dependent scale factors and b and c are two universal constants such that

$$b^2=\frac{3}{3-2\beta}\simeq1.2766,\ c=\frac{2\beta\delta-3}{3-2\beta}\simeq0.055. \tag{2.5}$$

The restricted cubic model equations for a number of thermodynamic properties (Sengers and Levelt Sengers, 1978) are summarized in Table I. Our choice is determined by the observation that this model contains only two system-dependent scale factors, as required by the hypothesis of critical-point universality, and that it leads to simple parametric equations for the compressibility, and, hence, for the density profile. With the exponent values adopted above, the restricted cubic model implies the following values for the universal amplitude ratios

$$\frac{A}{A'}=0.52\,,\ \frac{\Gamma}{\Gamma'}=4.92\,,\ \Gamma D B^{\delta-1}=1.70\,,\frac{A\Gamma}{B^2}=0.056\,. \tag{2.6}$$

These values may be compared with the values $A/A'=0.51, \Gamma/\Gamma'=5.07, \Gamma D B^{\delta-1}=1.75, A\Gamma/B^2=0.059$ as estimated for the Ising model from series expansions (Aharony and Hohenberg, 1976) and with $A/A'=0.48$, $\Gamma/\Gamma'=4.80$, $\Gamma D B^{\delta-1}=1.6$, $A\Gamma/B^2=0.066$ as estimated for the Landau-Ginzburg-Wilson model from a perturbation expansion around four dimensions, commonly referred to as an ε expansion, where $\varepsilon=4-d$ (Aharony and Hohenberg, 1976; Bervillier, 1976). Thus the restricted cubic model approximates the universal amplitude ratios and, hence, the scaling function, to within the accuracy with which these quantities are currently known theoretically.

Another important quantity in the theory of critical phenomena is the range of the order parameter correlation function (Fisher, 1964, 1967). In terms of the restricted cubic model this correlation length may be represented by (Sengers and Levelt Sengers, 1978)

$$\xi=r^{-\nu}\xi_0 R(\theta)\,, \tag{2.7}$$

where $R(\theta)$ is an even function of θ such that

$$R(0)=1\,,\quad R(1)=\frac{\xi_0'}{\xi_0}\left(\frac{\Gamma}{\Gamma'}\right)^{\nu/\gamma}\,. \tag{2.8}$$

Series expansions for the Ising model (Tarko and Fisher, 1975) have yielded $R(1)=1.17$, while currently available ε-expansion results for the Landau–Ginzburg–Wilson model (Brézin *et al.*, 1976) imply $R(1)=1.16$. We thus approximate $R(\theta)$ by (Sengers and Levelt Sengers, 1978)

$$R(\theta)=1+0.16\theta^2\,. \tag{2.9}$$

The scale factor ξ_0 for the correlation length can be related to the thermodynamic amplitudes B and Γ by

$$\xi_0(B^2 P_c/\Gamma k_B T_c)^{1/3}=0.69\pm0.04\,, \tag{2.10}$$

where k_B is Boltzmann's constant. This relationship follows from the hypothesis of two-scale-factor universality (Stauffer *et al.*, 1972; Hohenberg *et al.*, 1976) and it has been verified for Xe, CO_2, and SF_6 near the critical point (Sengers and Moldover, 1978b). Here we assume this relation to be valid for all fluids under consideration.

The correlation length, the compressibility, and the specific heat are analytic functions of the parametric variable θ, while they are all singular functions of the parametric variable r. Thus, as is customary, we shall use the dimensionless variable r as a suitable measure of "distance" from the critical point. The simple power laws represent asymptotic thermodynamic behavior in the vicinity of the critical point. In addition, there are correction terms whose relative contribution is proportional to r^{Δ}, where Δ is a correction-to-scaling exponent (Wegner, 1972); for Ising-like systems $\Delta\simeq0.5$. Hence, for an accurate description at the one percent level, the validity of a simple scaled equation of state with the theoretically predicted universal exponent values is restricted to a range $r\leq10^{-4}$, assuming that the nonuniversal amplitudes of the correction terms are of order unity. These limitations are confirmed by analyses of experimental data for fluids near the gas-liquid critical point (Ley-Koo and Green, 1977; Balfour *et al.*, 1977, 1978).

In Table II we present critical region parameters for Xe, CO_2, SF_6, and H_2O. For Xe, CO_2, SF_6 the cubic model parameters were obtained by adopting the exponent values $\beta=0.325$ and $\gamma=1.240$ and then determining the corresponding power-law amplitudes from the profile data obtained by Hocken and Moldover (1976). The parameters for H_2O were deduced from an analysis by Balfour *et al.* (1977, 1978) of the classical *PVT* data of Rivkin and coworkers, taking into account correction to scaling terms of a form predicted by the theory.

In Table III we present estimated critical region parameters for a number of other fluids. At this time, we do not know the parameters a and k for these other fluids nearly as well as for Xe, CO_2, SF_6, and H_2O. In an earlier correlation Levelt Sengers et al. (1976) determined the parameters a and k from experimental data "far from T_c" (i.e., $|\Delta T^*|>10^{-4}$) using a scaled equation of state with effective exponents $\beta=0.355$ and $\gamma=1.19$. Here we are concerned with the behavior closer to T_c, where the exponents $\beta=0.325$ and $\gamma=1.24$ must be used. We estimated the corresponding parameters a and k from those earlier presented by Levelt Sengers *et al.* assuming that the correction to scaling

TABLE II. Critical region parameters for Xe, CO_2, SF_6, and H_2O.[a]

	Critical point parameters			Cubic model parameters		Gravity scale factor	Correlation length amplitude	Refractive index
	P_c MPa	ρ_c kg/m^3	T_c K	k	a	$H_0\times10^{-3}$ m	$\xi_0\times10^{10}$ m	n_c
Xe	5.840	1110	289.72	0.89	15.4	0.536	1.9	1.137
CO_2	7.375	467	304.13	1.00	21.7	1.61	1.5	1.106
SF_6	3.761	730	318.69	1.01	22.0	0.525	1.9	1.091
H_2O	22.034	322	647.02	1.25	20.2	6.98	1.3	1.103

[a] Notes: $\alpha=0.11$ $\beta=0.325$ $\nu=0.63$ $b=1.130$
$\gamma=1.24$ $\delta=4.815$ $\eta=0.03$ $c=0.055$

TABLE III. Estimated critical region parameters for a number of fluids.[a]

	Critical point parameters			Cubic model parameters		Gravity scale factor	Correlation length amplitude	Refractive index
	P_c MPa	ρ_c kg/m^3	T_c K	k	a	$H_0 \times 10^{-3}$ m	$\xi_0 \times 10^{10}$ m	n_c
^{3}He	0.1168	41.5	3.31	0.67	4.4	0.287	2.6	1.011
^{4}He	0.2274	69.6	5.19	0.74	6.1	0.333	2.1	1.014
Ar	4.865	535	150.73	0.89	15.4	0.926	1.6	1.086
Kr	5.493	908	209.29	0.89	15.4	0.616	1.7	1.108
p-H_2	1.285	31.4	32.94	0.84	9.2	0.417	1.8	1.049
N_2	3.398	314	126.20	0.99	17.4	1.10	1.6	1.076
O_2	5.043	436	154.58	0.94	14.8	1.18	1.6	1.084
D_2O	21.66	357	643.89	1.25	20.2	6.18	1.3	1.103
NH_3	11.303	235	405.4	1.14	20.6	4.90	1.4	1.119
CH_4	4.595	163	190.56	0.99	16.3	2.88	1.7	1.102
C_2H_4	5.040	215	282.34	0.98	16.7	2.39	1.8	1.126
C_2H_6	4.872	206	305.33	1.03	19.3	2.40	1.8	1.119
C_3H_8	4.247	221	369.82	1.05	19.3	1.96	2.0	1.127

[a] Notes: $\alpha = 0.11$ $\beta = 0.325$ $\nu = 0.63$ $b = 1.130$
$\gamma = 1.24$ $\delta = 4.815$ $\eta = 0.03$ $c = 0.055$

terms for these fluids are of the same magnitude as those for the fluids quoted in Table II. In many cases the estimates are deduced from scant experimental data. Moreover, the magnitude of the correction to scaling terms will in fact differ from fluid to fluid. In particular, it has been suggested that for helium these correction terms may be substantially larger than for other fluids (Behringer *et al.*, 1976). Thus the parameters in Table III should only be considered as informed estimates, but with limited accuracy. Nevertheless, they do allow us to estimate to what extent the size of the gravity effects may vary with the choice of fluid.

In all cases we estimated the correlation length scale factor ξ_0 from the equation of state parameters using the two-scale-factor universality relation (2.10). The values thus obtained for ξ_0 are in satisfactory agreement with experimental correlation length data reported for helium (Tominaga, 1974; Roe and Meyer, 1978), argon (Lin and Schmidt, 1974), xenon (Swinney and Henry, 1973), carbon dioxide (Lunacek and Cannell, 1971), and sulfur hexafluoride (Cannell, 1975). For further details the reader is referred to an earlier review (Sengers and Levelt Sengers, 1978).

In this paper we shall make all quantitative calculations of the gravity effects using xenon as an example. From the equations presented, the gravity effects may be readily estimated for other fluids using the parameters listed in Tables II and III.

III. GRAVITY-INDUCED PROFILES

As a consequence of the presence of the gravitational field, the local value of the density in a near-critical fluid will vary with the vertical coordinate z. To evaluate the resulting practical limitations, we assume that the local chemical potential $\mu(\rho(z), T)$ at each level z in the fluid equals the chemical potential of a system with uniform density $\rho = \rho(z)$ at temperature T in the absence of gravity. The region around the critical point, where this assumption ceases to be valid and where gravity affects the local values of the thermodynamic properties directly, will be considered in Sec. VII.

In this approximation the variation of the local chemical potential $\mu(\rho(z), T)$, taken per unit mass, simply compensates for the variation of the gravitational potential gz, so that

$$\mu(\rho(z), T) - \mu(\rho(z_0), T) = -g(z - z_0) = -g\Delta z\,, \tag{3.1}$$

where z_0 is a reference level in the fluid. It is convenient to take the reference level z_0 such that $\rho(z_0) = \rho_C$ and to introduce the quantity (Levelt Sengers, 1975)

$$H_0 = P_c/\rho_c g_0\,, \tag{3.2}$$

which represents a gravity scale height of the fluid in the earth's gravitational field with $g_0 = 9.81\text{m/s}^2$. Then

$$\Delta z = -(H_0/g^*)\,\Delta\mu^*\,, \tag{3.3}$$

where $\Delta\mu^*$ is the reduced chemical potential difference defined in the preceding section and

$$g^* = g/g_0 \tag{3.4}$$

the reduced gravitational acceleration constant. The values for the gravity scale height H_0 for a number of fluids are included in Tables II and III. Density gradients in earth-bound experiments can be neglected as long as

$$H_0 \gg h\,(\partial\rho^*/\partial\mu^*)_T = h\chi_T^*\,, \tag{3.5}$$

where h is the height of the sample volume. However, due to the strong divergence of the compressibility χ_T^*, this condition will always be violated close to the critical point of fluids.

At the critical temperature $T = T_c$, the density profile can be represented asymptotically by the simple power law

$$\Delta z = -(H_0/g^*) D\Delta\rho^* |\Delta\rho^*|^{\delta-1}\,. \tag{3.6}$$

In Fig. 1 we show the density as a function of height for xenon at the critical temperature at three different values of the magnitude of the gravitational fields. The

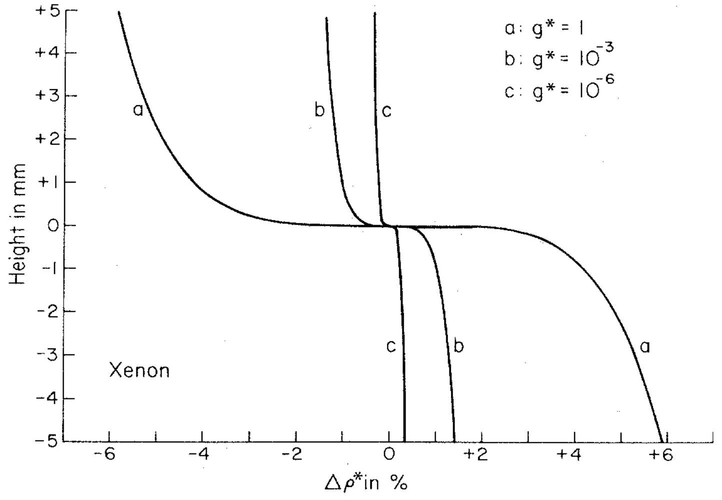

FIG. 1. Density as a function of height in xenon at the critical temperature.

values $g^*=10^{-3}$ and $g^*=10^{-6}$ correspond to the gravitational levels that one may hope to reach in the projected space laboratory facilities under the worst and optimum conditions (Dodge *et al.*, 1975; Shapland, 1976; Morrell, 1977). In earth-bound experiments, the density in a cell of 1cm height will vary by more than 10%; in a cell of 1mm height the density variation is still more than 7%. On the other hand, at $g^*=10^{-6}$ the inhomogeneity in the density is reduced to fractions of a percent.

It follows from Eqs. (2.4) and (3.3) that at a given temperature ΔT^* the density profile can be calculated from the parametric equations

$$r=\Delta T^*/(1-b^2\theta^2)\geqslant 0\,, \tag{3.7a}$$

$$\Delta\rho^*=r^{\beta}k\theta(1+c\theta^2)\,, \tag{3.7b}$$

$$\Delta z=-(H_0/g^*)ar^{\beta\delta}\theta(1-\theta^2)\,. \tag{3.7c}$$

In the restricted cubic model the local value of the density gradient is given by the simple expression

$$\left(\frac{\partial\rho^*}{\partial z}\right)_T=-\frac{g^*}{H_0}\chi_T^*=-\frac{g^*}{H_0}\Gamma r^{-\gamma}\,. \tag{3.8}$$

We shall also need the rate with which the local compressibility and the local value of the correlation length ξ will vary with the vertical position z

$$\left(\frac{\partial\chi_T^*}{\partial z}\right)_T=-\frac{g^*}{H_0}\chi_T^*\left(\frac{\partial\chi_T^*}{\partial\rho^*}\right)_T\,, \tag{3.9}$$

$$\left(\frac{\partial\xi}{\partial z}\right)_T=-\frac{g^*}{H_0}\chi_T^*\left(\frac{\partial\xi}{\partial\rho^*}\right)_T\,. \tag{3.10}$$

The parametric equations for $(\partial\chi_T^*/\partial\rho^*)_T$ and $(\partial\xi/\partial\rho^*)_T$ are included in Table I.

IV. AVERAGING ERRORS DUE TO FINITE SAMPLE HEIGHT

In critical phenomena experiments one wants to determine various physical properties within a certain desired precision. Frequently, the desired precision may be expressed as a small fraction p of the quantity to be measured. However, experimental methods to measure fluid properties require the use of experimental probes of finite height. The experimentally observed behavior of fluid properties in the vicinity of the critical point is rounded due to the fact that the property to be measured is averaged over a collection of thermodynamic states with different densities, limiting the precision attainable in practice. A precise calculation of the densities and temperatures at which gravitational averaging becomes severe would involve the following steps: (a) Identify the quantity to be measured, say Q, and the precision p with which the quantity is to be determined. (b) Examine the measurement technique to determine over what range of height $0\leqslant z\leqslant h$ it averages and with what function, say $w(z)$, it weights the quantity Q at each height. (c) The range of densities and temperatures where gravity-induced averaging errors can be neglected is then determined by the inequality

$$\left|\frac{1}{h}\int_0^h dz w(z)Q(\rho(z),T)-Q(\rho(h/2),T)\right|\leqslant pQ(\rho(h/2),T)\,. \tag{4.1}$$

Here we have assumed that the weighted average of Q which the experiment measures will be assigned to the thermodynamic state $(\rho(h/2),T)$ at the midheight of the experimental probe. A somewhat more complex calculation is required when Q is a quantity measured by experimentally taking a temperature derivative, such as the constant-volume specific heat.

Condition (4.1) is also satisfied when $w(z)=1$ and the quantity Q happens to vary linearly with z. In practice, once the fluid properties begin to vary as a function of height, the variation rapidly becomes nonlinear when the critical point is approached. In order to obtain estimates for the gravity-affected range covering a large variety of experiments we shall take the weighting function to be constant and simply require that the variation of the quantity Q over the averaging height h be smaller than pQ

$$\left|Q\left(\rho\left(z+\frac{h}{2}\right),T\right)-Q\left(\rho\left(z-\frac{h}{2}\right),T\right)\right|\leqslant pQ(\rho(z),T)\,. \tag{4.2}$$

To make the estimates quantitative, we shall typically assume a desired resolution of one percent, i.e., $p = 0.01$. As representative fluid properties we consider in this section the density, compressibility, and specific heat.

A. Density measurements

As a first example we consider some methods for measuring the equation of state. In classical equation of state experiments one measures the pressure as a function of temperature for a given quantity of the fluid. Hence one obtains the pressure at a certain level as a function of the average density in a cell of a given height h. Another practical instrument for measuring fluid densities is a float densimeter (Maass and Geddes, 1937; Naumenko *et al.*, 1967; Artyukhovskaya *et al.*, 1970; Greer *et al.*, 1974). In such an instrument the buoyant force on a float of known density is balanced with a spring or magnetic restoring force. The deflection of the spring or the current in the electromagnet is then a measure of the fluid density averaged over the height h of the float. A third method for measuring the density of a fluid is to measure the dielectric constant as a function of height (Weber, 1970; Thoen and Garland, 1974), using the known relationship between dielectric constant and the density. Here the averaging distance is determined by the distance h between the capacitor plates.

In order for these methods to yield an adequate resolution we require that the variation of the density over the averaging height be within a desired precision

$$|\rho^*(z+\frac{h}{2})-\rho^*(z-\frac{h}{2})| \leq p\rho^*(z) \simeq p . \qquad (4.3)$$

Approximating (4.3) by $h|(\partial\rho^*/\partial z)_T| \leq p$ we conclude from Eq. (3.8) that

$$\chi_T^* \leq \frac{pH_0}{g^*h} , \qquad (4.4)$$

or, in terms of the parametric "distance" variable r,

$$r \geq r_{\min} = \left(\frac{g^*h}{pH_0}\Gamma\right)^{1/\gamma} . \qquad (4.5)$$

If this condition is not satisfied, i.e., in a region around the critical point where $r < r_{\min}$, density measurements will be seriously rounded by gravity effects. As an example we show in Fig. 2 this region for xenon when the density is averaged over a height as small as 1mm, assuming $p = 0.01$. The gravity-affected range depends on the nature of the particular fluid through the factor $(\Gamma/H_0)^{1/\gamma}$, which may be calculated from the information in Tables I, II, and III. We note that the gravity-affected range $r_{\min}$ in helium is about four times larger and in steam about three times smaller than that in xenon.

In order to characterize the gravity-affected range in a simple way, we define $\Delta T^*_{\min}$ as the smallest temperature difference at the critical density $\rho = \rho_c$ accessible before gravitationally induced averaging errors become serious. Similarly, we define $\Delta\rho^*_{\min}$ as the minimum density difference accessible at the critical temperature $T = T_c$ without serious gravitationally induced errors. It follows from Eq. (4.5) that

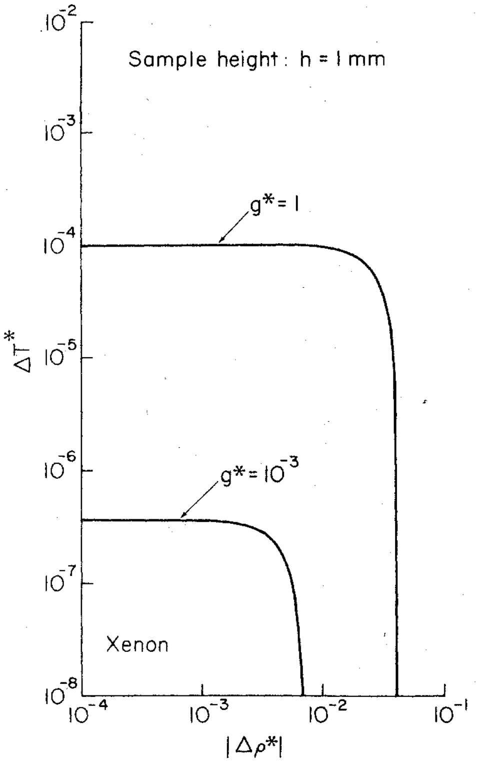

FIG. 2. Range of temperatures and densities around the critical point of xenon where the local density varies by more than 1% over a height of 1 mm.

$$\Delta T^* \geq \Delta T^*_{\min} = \left(\frac{g^*h}{pH_0}\Gamma\right)^{1/\gamma} , \qquad (\rho = \rho_c) , \quad (4.6a)$$

$$|\Delta\rho^*| \geq |\Delta\rho^*_{\min}| = \left(\frac{g^*h}{pH_0}\frac{1}{\delta D}\right)^{\beta/\gamma} , \qquad (T = T_c) . \quad (4.6b)$$

For xenon we obtain the estimates

$$\Delta T^* \geq \Delta T^*_{\min} = 6.3\times 10^{-4}\left(\frac{g^*h}{p}\right)^{0.81} , \qquad (\rho = \rho_c) , \quad (4.7a)$$

$$|\Delta\rho^*| \geq |\Delta\rho^*_{\min}| = 0.075\left(\frac{g^*h}{p}\right)^{0.26} , \qquad (T = T_c) , \quad (4.7b)$$

where the averaging height h is to be expressed in meters. Results thus obtained for xenon at different values of g^*, taking $p = 0.01$, are given in Table IV. For averaging heights as small as 1mm, measurement in earth-bound experiments become blurred by gravity effects at temperatures $\Delta T^* < 10^{-4}$ which corresponds in xenon to $T - T_c \simeq 0.03$ °C. For comparison we note that with state of the art techniques (Sarid and Cannell, 1974; Dratler, 1974; Hocken and Moldover, 1976) it is possible to reach a temperature stability of the order of 10 microdegrees, which means that in principle one could carry out a measurement with values of ΔT^* as small as 10^{-7}.

B. Compressibility measurements

In practice one is interested not only in the equation of state itself, but also in its derivatives and, in par-

TABLE IV. Values of $\Delta T^*_{\min}$ and $\Delta\rho^*_{\min}$ for xenon where gravity effects in density measurements become of the order of 1%.

	$h=10^{-2}$ m		$h=10^{-3}$ m		$h=10^{-4}$ m	
	$\rho=\rho_c$ $\Delta T^*_{\min}$	$T=T_c$ $\Delta\rho^*_{\min}$	$\rho=\rho_c$ $\Delta T^*_{\min}$	$T=T_c$ $\Delta\rho^*_{\min}$	$\rho=\rho_c$ $\Delta T^*_{\min}$	$T=T_c$ $\Delta\rho^*_{\min}$
$g^*=1$	6.3×10^{-4}	7.5×10^{-2}	9.9×10^{-5}	4.1×10^{-2}	1.5×10^{-5}	2.2×10^{-2}
$g^*=10^{-3}$	2.4×10^{-6}	1.2×10^{-2}	3.7×10^{-7}	6.7×10^{-3}	5.9×10^{-8}	3.6×10^{-3}
$g^*=10^{-6}$	9.1×10^{-9}	2.0×10^{-3}	1.4×10^{-9}	1.1×10^{-3}	2.2×10^{-10}	6.0×10^{-4}

ticular, in the compressibility, which is the response function associated with the order parameter. To obtain this quantity with adequate resolution, it is more realistic to require that the variation of the *compressibility* over the sampling height be smaller than the desired precision

$$|\chi_T^*(z+\frac{h}{2})-\chi_T^*(z-\frac{h}{2})| \leq p\chi_T^*(z)\,. \tag{4.8}$$

At densities not too close to the critical density we approximate (4.8) by

$$h\left|\left(\frac{\partial\chi_T^*}{\partial z}\right)_T\right| \leq p\chi_T^*\,. \tag{4.9}$$

In terms of the cubic model parameters we thus obtain

$$r \geqslant r_{\min} = \left(\frac{g^*h}{H_0ap}\right)^{1/\beta\delta}\left|\frac{2b^2\gamma\theta}{q(\theta)}\right|^{1/\beta\delta}. \tag{4.10}$$

This equation determines a range $r=r_{\min}(\theta)$ inside which compressibility measurements are affected by gravity-induced averaging errors. In terms of ΔT^* and $\Delta\rho^*$ this region is shown in Fig. 3 for xenon for an averaging height of 1mm, again taking $p=0.01$. At the critical temperature, Eq. (4.10) implies

$$|\Delta\rho^*| \geqslant |\Delta\rho^*_{\min}| = \left(\frac{g^*h}{H_0pD}\,\frac{\gamma}{\beta\delta}\right)^{1/\delta}, \qquad (T=T_c)\,. \tag{4.11}$$

At the critical density $\rho=\rho_c$, $(\partial\chi_T^*/\partial z)_T=0$ and the approximation (4.9) is no longer adequate, so we must return to Eq. (4.8). At a given temperature the compressibility χ_T^* varies with the parametric variable θ as $(1-b^2\theta^2)^\gamma$. Near the critical density corresponding to $\theta \ll 1$, the distance Δz_p over which the compressibility will change by a factor p is determined by the condition $1-p=(1-b^2\theta_p^2)^\gamma \simeq 1-\gamma b^2\theta_p^2$, so that from Eq. (3.7c)

$$|\Delta z_p| \simeq \frac{H_0}{g^*}\,\frac{a}{b}\left(\frac{p}{\gamma}\right)^{1/2}(\Delta T^*)^{\beta\delta}\,. \tag{4.12}$$

In order to obtain the desired precision this distance should be equal to or larger than the height h of the experimental probe. We thus obtain the estimate

$$\Delta T^* \geqslant \Delta T^*_{\min} = \left[\frac{g^*h}{H_0}\,\frac{b}{a}\left(\frac{\gamma}{p}\right)^{1/2}\right]^{1/\beta\delta}, \qquad (\rho=\rho_c)\,. \tag{4.13}$$

For xenon the conditions (4.11) and (4.13) become

$$|\Delta\rho| \geqslant |\Delta\rho^*_{\min}| = 0.17\ \frac{g^*h}{p}^{0.21}, \qquad (T=T_c)\,, \tag{4.14a}$$

$$\Delta T^* \geqslant \Delta T^*_{\min} = 3.6\times10^{-3}\left(\frac{g^*h}{\sqrt{p}}\right)^{0.64}, \qquad (\rho=\rho_c)\,, \tag{4.14b}$$

where h is again to be expressed in meters. Equation (4.14b) determines the intercepts with the temperature axis in Fig. 3 for small values of $\Delta\rho^*$.

The ranges $\Delta T^*_{\min}$ and $\Delta\rho^*_{\min}$ for xenon where compressibility measurements are affected by gravitational averaging at various gravitational levels are presented in Table V. We not only list the values for averaging heights of 1cm and 1mm, but for future reference have included the range corresponding to an averaging height of 0.1mm.

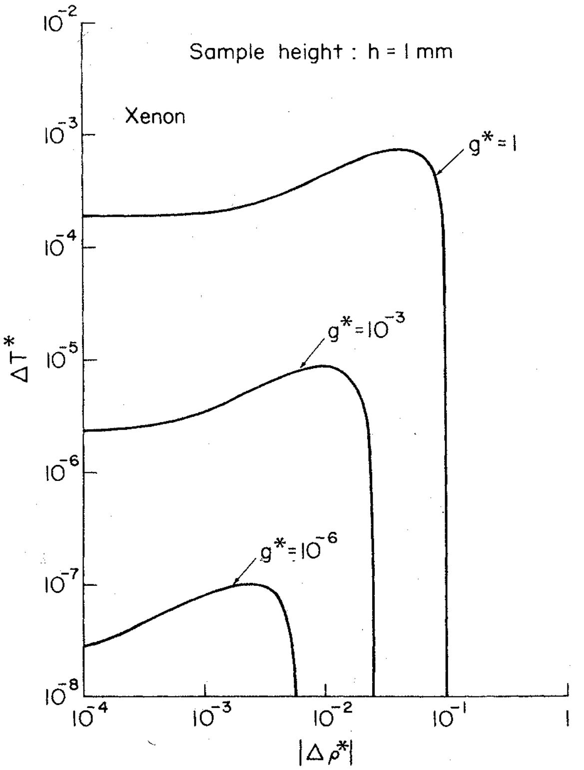

FIG. 3. Range of temperatures and densities around the critical point of xenon where the local compressibility varies by more than 1% over a height of 1 mm.

TABLE V. Values of $\Delta T^*_{\min}$ and $\Delta\rho^*_{\min}$ for xenon where gravity effects in compressibility measurements become of the order of 1%.

	$h=10^{-2}$ m		$h=10^{-3}$ m		$h=10^{-4}$ m	
	$\rho=\rho_c$ $\Delta T^*_{\min}$	$T=T_c$ $\Delta\rho^*_{\min}$	$\rho=\rho_c$ $\Delta T^*_{\min}$	$T=T_c$ $\Delta\rho^*_{\min}$	$\rho=\rho_c$ $\Delta T^*_{\min}$	$T=T_c$ $\Delta\rho^*_{\min}$
$g^*=1$	8.4×10^{-4}	1.7×10^{-1}	1.9×10^{-4}	1.0×10^{-1}	4.4×10^{-5}	6.5×10^{-2}
$g^*=10^{-3}$	1.0×10^{-5}	4.0×10^{-2}	2.3×10^{-6}	2.5×10^{-2}	5.3×10^{-7}	1.5×10^{-2}
$g^*=10^{-6}$	1.2×10^{-7}	9.6×10^{-3}	2.8×10^{-8}	5.9×10^{-3}	6.5×10^{-9}	3.7×10^{-3}

C. Specific heat measurements

The situation is more complicated when one wants to evaluate the effects of gravity in the measurements of the specific heat C_v. In the presence of a gravitational field one does not simply measure a specific heat averaged over the range of local densities in the cell; one needs also to account for thermal contributions associated with the rearrangement of the density profile upon change of temperature. Analysis of the effect of gravity on specific heat measurements have been made by a number of authors (Chashkin *et al.*, 1967; Berestov *et al.*, 1969, 1973; Berestov and Malyshenko, 1970; Schmidt, 1971; Hohenberg and Barmatz, 1972; Lipa *et al.*, 1977). Here we adopt the detailed results obtained by Hohenberg and Barmatz (1972).

Hohenberg and Barmatz derived estimates of $\Delta T^*_{\min}$ for three different fluids (Xe, CO_2, ^{4}He) and for three different sample heights (0.1 cm, 1 cm, 10 cm), where the gravity-induced corrections become of the order of 10%. In order to scale these results with the magnitude of the gravitational field we note that these estimates may be approximated by the simple rule that the gravity-affected range for specific heat measurements is about 0.4 as large as the range evaluated above for compressibilities averaged over the same sample height. That is, from Eq. (4.13) we estimate the gravity-affected range for specific heat measurements by

$$\Delta T^* \geqslant \Delta T^*_{\min} \simeq \left[0.23\frac{g^*h}{H_0}\,\frac{b}{a}\left(\frac{\gamma}{p}\right)^{1/2}\right]^{1/\beta\delta}, \quad (\rho=\rho_c)\,. \qquad (4.15)$$

In Table VI we compare the values of $\Delta T^*_{\min}$ listed by Hohenberg and Barmatz with the values evaluated from (4.15) using the parameters given in Tables II and III. While a more precise formula would also depend on the magnitude of the background specific heat in the absence of critical fluctuations, we conclude from the data in Table VI that our simple rule yields adequate estimates for the purpose. That is, from the work of Hohenberg and Barmatz we find that the gravity-affected range scales with $h^{1/\beta\delta}$ and hence with $(g^*h)^{1/\beta\delta}$.

As mentioned in Sec. II the validity of simple asymptotic power-law behavior is restricted to a temperature range of the order of $\Delta T^* < 10^{-4}$. In this section we have considered measurements of density, compressibility, and specific heat as representative thermophysical properties. From the information provided it is evident that any thermophysical property which requires an experimental probe with a height of the order of millimeters cannot be accurately measured in this range on earth without serious rounding effects due to gravity. One may, of course, attempt to correct the experiments for these gravity effects. However, the resolution yielded by such procedures is hampered by the fact that one does not have accurate *a priori* knowledge of either the constants in the asymptotic equations or of the magnitude of the correction to scaling contributions. The temperature range accessible without gravity-induced errors scales as $g^{*1/\beta\delta} = g^{*0.64}$. Hence, a substantial improvement in temperature resolution is in principle possible with experiments in a low-gravity environment, assuming the other experimental conditions remain competitive with earth-bound experiments.

V. LIMITATIONS OF OPTICAL EXPERIMENTS

A. Beam bending

The gravity-induced density profiles in the critical region of fluids imply that the refractive index n also varies as a function of height. Since the Lorentz–Lorenz function $(n^2-1)/(n^2+2)$ is to a good approximation proportional to the density, the refractive index near the critical density may be represented by (Estler *et al.*, 1975)

TABLE VI. Values of $\Delta T^*_{\min}$ at which gravity effects in specific heat measurements become of the order of 10% ($g^*=1$).

	Xe		CO_2		^{4}He	
Sample height	$\Delta T^*_{\min}$ [a]	$\Delta T^*_{\min}$ [b]	$\Delta T^*_{\min}$ [a]	$\Delta T^*_{\min}$ [b]	$\Delta T^*_{\min}$ [a]	$\Delta T^*_{\min}$ [b]
$h=0.001$m	3.4×10^{-5}	3.6×10^{-5}	1.5×10^{-5}	1.4×10^{-5}	8.2×10^{-5}	8.8×10^{-5}
$h=0.01$m	1.5×10^{-4}	1.6×10^{-4}	6.7×10^{-5}	6.2×10^{-5}	3.7×10^{-4}	3.8×10^{-4}
$h=0.1$m	6.8×10^{-4}	6.8×10^{-4}	$3\ \ \times10^{-4}$	2.7×10^{-4}	1.7×10^{-3}	1.7×10^{-3}

[a] From Table II in Hohenberg and Barmatz, 1972.
[b] From Eq. (4.15) with $p=0.1$.

$$n = n_c + n_c' \Delta\rho^* , \tag{5.1}$$

$$\left(\frac{\partial n}{\partial z}\right)_T = n_c' \left(\frac{\partial \rho^*}{\partial z}\right)_T = -n_c' \frac{g^*}{H_0} \chi_T^* , \tag{5.2}$$

where n_c is the value of the refractive index at the critical point and where

$$n_c' = (n_c^2 - 1)(n_c^2 + 2)/6n_c . \tag{5.3}$$

Estimated values for the refractive index n_c at optical wavelengths of about 0.6 μm are included in Tables II and III. For a number of fluids direct experimental evidence for n_c is available [xenon (Chapman *et al.*, 1968), carbon dioxide (Levelt Sengers *et al.*, 1971), sulfur hexafluoride (Balzarini and Ohrn, 1972; Cannell, 1977a; Rathjen and Straub, 1977), helium (Doiron and Meyer, 1978; Edwards and Woodbury, 1963), argon and krypton (Pings, private communication), and hydrogen (Diller, 1968)]. For the other fluids we took the refractive indices at standard temperature and pressure (International Critical Tables of Numerical Data in Physics, Chemistry, and Technology, 1950; Landolt-Börnstein, 1962) and converted them to the critical density using the Lorentz-Lorenz relation. The coefficient n_c' is a measure of the efficiency with which density gradients are converted into refractive index gradients (Hocken and Moldover, 1978).

In the previous section we considered gravity effects in experiments where the averaging height is of the order of millimeters. This averaging height can be further reduced for those properties that can be measured by optical methods. A primary example is measuring the equation of state by determining the refractive index or the refractive index gradient as a function of height. Several investigators have made pioneering studies of this kind in the fifties and the sixties (Lorentzen, 1953; Palmer, 1954; Schmidt and Traube, 1962; Straub, 1967). In view of the awkward arrangements due to the need for windows, optical experiments have often been affected by thermal gradients and the method has only recently become suitable for quantitative interpretations (Artyukhovskaya *et al.*, 1971, 1973; Estler *et al.*, 1975; Hocken and Moldover, 1976).

A sensitive experimental method was developed by Wilcox and Balzarini (1968) and refined by Estler *et al.* (1975). This method, originally proposed by Gouy (1880), uses the Fraunhofer diffraction pattern produced when light traverses a fluid in which refractive index gradients exist. If a thin slab of fluid is illuminated by a plane wave, light rays crossing the fluid are bent downward by an angle proportional to the refractive index gradient and hence the density gradient. Furthermore, these rays are phase shifted by an amount proportional to their optical path in the fluid, which is related to the local density. To a good approximation the fluid density profiles are antisymmetric with respect to the inflection point, while the gradient is symmetric (c.f. Fig. 1). Therefore rays entering at equal distances above and below the plane of symmetry bend through the same angle, but experience a relative phase shift proportional to the density difference between the two levels. From the interferometric pattern produced one can deduce the relationship between local gradient and density. Hocken and Moldover (1976) used the method to determine the equation of state of xenon, carbon dioxide, and sulfur hexafluoride at values of the parametric variable r approximately between 10^{-4} and 10^{-5}; the equation of state parameters deduced from these data are included in Table II.

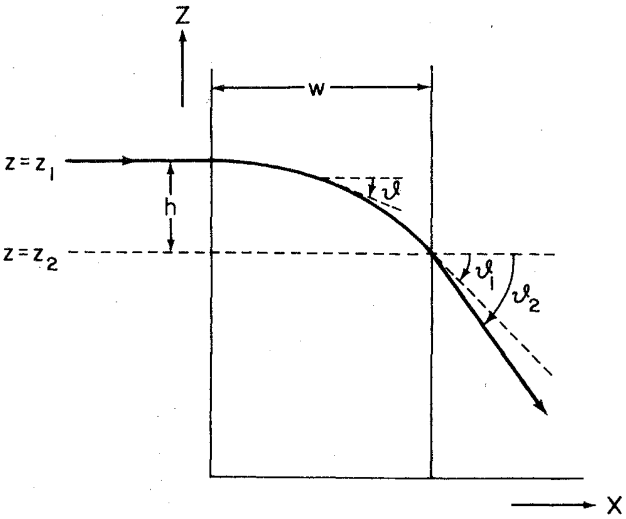

FIG. 4. Schematic representation of a light ray bent by a refractive index gradient in the fluid.

In Fig. 4 we consider schematically the path of a light ray incident in the X direction passing through a fluid stratified in the Z direction. The angle of the direction of the light ray with the X direction is indicated by ϑ. The final deflection angles of the ray just prior to and just after leaving the cell are ϑ_1 and ϑ_2, respectively; these angles are related by $\sin\vartheta_2 = n \sin\vartheta_1$, where n is the local refractive index of the fluid.

From the generalization of Snell's law to light propagation in a stratified medium (Born and Wolf, 1975), and assuming that the angle of deflection ϑ is small, it follows that the points on the light path *inside* the fluid satisfy the differential relations

$$\vartheta d\vartheta = \frac{1}{n}\frac{dn}{dz} dz = -\frac{1}{n}\frac{dn}{dz} \vartheta dx . \tag{5.4}$$

When the quantity $n^{-1}dn/dz$ is constant along the path, these relations can be readily integrated at constant temperature to yield

$$\vartheta_1 = -\frac{w}{n}\frac{dn}{dz} \simeq w \frac{n_c'}{n_c}\frac{g^*}{H_0} \chi_T^* , \tag{5.5}$$

$$h = -\frac{w^2}{2n}\frac{dn}{dz} \simeq \frac{w^2}{2}\frac{n_c'}{n_c}\frac{g^*}{H_0} \chi_T^* , \tag{5.6}$$

where w is the width of the fluid layer and where h is now the net vertical distance traversed by the light ray as a consequence of beam bending. Hence the total deflection of the light ray is proportional to the local compressibility $\chi_T^*(z)$. When the quantity $n^{-1}dn/dz$ is no longer constant, it follows from Eq. (5.4) that

$$\vartheta_1^2 = 2\int_{z_1}^{z_2} \left(\frac{1}{n}\frac{dn}{dz}\right) dz . \tag{5.7}$$

Thus we conclude that the deflected ray will no longer carry information about the value of the local compressibility at a particular level when the gradient $n^{-1}dn/dz \simeq (n_c'/n_c)(g^*/H_0)\chi_T^*$ begins to vary significantly over the height $h = z_1 - z_2$. This condition poses a limitation on *any* optical experiment, when the system is in thermodynamic equilibrium in the presence of gravity. The magnitude of the effect depends on the width of the fluid layer and has therefore been referred to as "thick cell error" (Wilcox and Balzarini, 1968; Estler *et al.*, 1975).

Thick cell errors will be negligible when

$$|\chi_T^*(z+\frac{h}{2}) - \chi_T^*(z-\frac{h}{2})| \leq p\chi_T^*(z)\,, \tag{5.8}$$

where the averaging height h to a good approximation is now given by Eq. (5.6). For densities not too close to ρ_c, we approximate (5.8) by (4.8)

$$h\frac{g^*}{H_0}\left|\left(\frac{\partial\chi_T^*}{\partial\rho^*}\right)_T\right| \simeq \frac{w^2}{2}\frac{n_c'}{n_c}\left(\frac{g^*}{H_0}\right)^2\chi_T^*\left|\left(\frac{\partial\chi_T^*}{\partial\rho^*}\right)_T\right| \leq p\chi_T^*. \tag{5.9}$$

In terms of the cubic model parameters we thus obtain

$$r \geq r_{\min} = \left[\left(\frac{g^*w}{H_0}\right)^2\frac{1}{p}\frac{n_c'}{n_c}\frac{k}{a^2}\left|\frac{b^2\gamma\theta}{q(\theta)}\right|\right]^{1/(\gamma+\beta\delta)}. \tag{5.10}$$

In particular at the critical temperature we obtain

$$|\Delta\rho^*| \geq |\Delta\rho^*_{\min}| = \left[\left(\frac{g^*w}{H_0}\right)^2\frac{1}{p}\frac{n_c'}{n_c}\frac{\gamma}{2\beta\delta^2 D}\right]^{\beta/(\gamma+\beta\delta)}, \quad (T=T_c)\,. \tag{5.11}$$

In order to estimate $\Delta T^*_{\min}$ at $\rho=\rho_c$, we note that the distance Δz_p over which the compressibility changes from χ_T^* to $(1-p)\chi_T^*$ is given by Eq. (4.12). For averaging effects to be negligible, this distance should be larger than the height $h \simeq (\omega^2/2)(n_c'/n_c)(g^*/H_0)(k/a) \times (\Delta T^*)^{-\gamma}$ so that

$$\Delta T^* \geq \Delta T^*_{\min} = \left[\left(\frac{g^*w}{H_0}\right)^2\frac{kb}{2a^2}\left(\frac{\gamma}{p}\right)^{1/2}\right]^{1/(\gamma+\beta\delta)}, (\rho=\rho_c). \tag{5.12}$$

For xenon these estimates become

$$|\Delta\rho^*| \geq |\Delta\rho^*_{\min}| = 0.085\left(\frac{g^{*2}w^2}{p}\right)^{0.12}, \quad (T=T_c), \tag{5.13a}$$

$$\Delta T^* \geq \Delta T^*_{\min} = 6.2\times10^{-4}\left(\frac{g^{*2}w^2}{\sqrt{p}}\right)^{0.36}, \quad (\rho=\rho_c)\,, \tag{5.13b}$$

where w is to be expressed in meters.

In Table VII we present the resulting values for xenon at various gravitational levels for cells with a thickness of 1cm and 1mm, taking $p = 0.01$. In Table VIII we present estimated values of the value $r_{\min}$ of the distance parameter r for Xe, CO_2, and SF_6 where the compressibility begins to vary by 10% along the optical path in earth-bound experiments. The estimates correspond to a cell thickness of 3mm, which is the minimum cell thickness with which optical equation of state experiments near the gas-liquid critical point have thus far been performed (Hocken and Moldover, 1976). These estimated values of $r_{\min}$ are of the same order of magnitude as the minimum distance actually approached in the interferometric experiments of Hocken and Moldover (1976); for smaller values of r they noted rapidly increasing deviations of the data from scaling law behavior. We conclude that in these experiments the critical point was approached as close as one can go without serious "thick cell errors" due to gravity.

TABLE VII. Values of $\Delta T^*_{\min}$ and $\Delta\rho^*_{\min}$ for xenon where the compressibility varies by 1% along the path of a light beam as a result of beam bending.

	$w=10^{-2}$m		$w=10^{-3}$m	
	$\rho=\rho_c$ $\Delta T^*_{\min}$	$T=T_c$ $\Delta\rho^*_{\min}$	$\rho=\rho_c$ $\Delta T^*_{\min}$	$T=T_c$ $\Delta\rho^*_{\min}$
$g^*=1$	5.3×10^{-5}	5.0×10^{-2}	1.0×10^{-5}	2.9×10^{-2}
$g^*=10^{-3}$	3.9×10^{-7}	1.0×10^{-2}	7.5×10^{-8}	5.9×10^{-3}
$g^*=10^{-6}$	2.8×10^{-9}	2.0×10^{-3}	5.4×10^{-10}	1.2×10^{-3}

TABLE VIII. Minimum values of the distance parameter r for optical experiments in Xe, CO_2, and SF_6 in a 3 mm thick cell ($g^*=1$).

		Xe	CO_2	SF_6
$(T=T_c)$	$r_{\min}$[a]=	3.4×10^{-5}	1.2×10^{-5}	2.5×10^{-5}
$(\rho=\rho_c)$	$r_{\min}$[b]=	1.5×10^{-5}	0.5×10^{-5}	1.1×10^{-5}
(exp)	$r_{\min}$[c]=	1.5×10^{-5}	1.0×10^{-5}	1.2×10^{-5}

[a] From Eq. (5.11) with $p=0.1$.
[b] From Eq. (5.12) with $p=0.1$.
[c] From Hocken and Moldover, 1976.

In Fig. 5 we show the range of temperatures and densities around the critical point of xenon where the local compressibility begins to vary by 1% along the path of a light beam passing through a fluid layer with a width of 3 mm. On comparing these results with the estimates presented in the preceding section (c.f. Fig. 3), we note that the optical interferometric experiments allow us to approach the critical point one decade closer in r than other experiments which require averaging over distances of the order of millimeters.

This increase in accessible range has turned out to be very important, since experiments in this range have shown that the critical exponents of fluids do indeed approach the values attributed to the universality class of Ising-like systems. However, since all earth-bound experiments with fluids in true thermodynamic equilibrium become affected by gravitational averaging errors at temperatures ΔT^* of the order of 10^{-5}, it will be difficult to establish, for example over three decades in ΔT^*, whether the apparent critical exponents of fluids near the critical point have indeed reached their asymptotic values. This is one of the reasons why critical phenomena experiments in a space laboratory may be of scientific interest.

The accessible range in optical experiments could, in principle be extended by using thinner fluid samples. However, in samples less than 10 μm the measurements may become distorted by the presence of critical wetting layers on the window cells as discussed by Cahn (1977). Furthermore the use of thinner cells leads to diffraction patterns with very small deflection angles. Limited

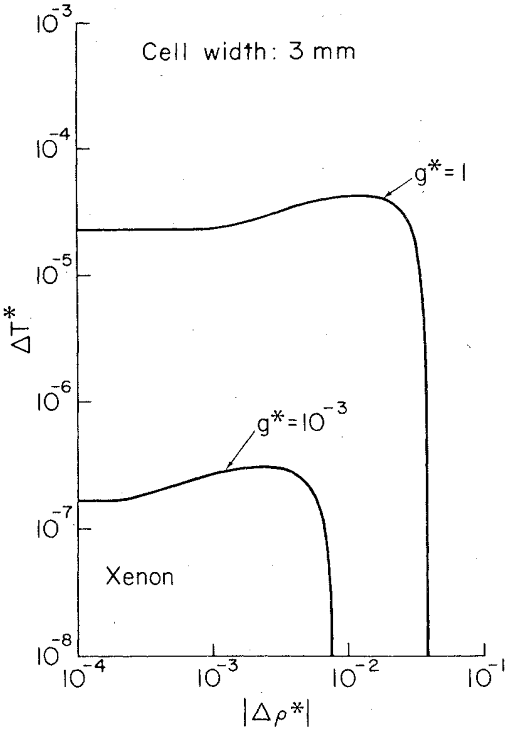

FIG. 5. Range of temperatures and densities around the critical point of xenon where the local compressibility varies by more than 1% over the path of a light ray in a cell with a thickness of 3 mm.

angular resolution makes it difficult to cover a range of temperatures of more than one decade with a cell of given thickness.

From Eqs. (5.10) and (5.12) we conclude that the range of beam-bending effects scales as $(g^*w)^{2/(\gamma+\beta\delta)} \simeq (g^*w)^{0.7}$. The specific interferometric method developed by Wilcox *et al.* does not appear suitable for application at low gravitational levels. This method requires a very steady g^* for extended periods of time, a condition not likely to be available in a manned space laboratory.

B. Light-scattering experiments

Near the critical point long-range fluctuations in the density are present in the fluid and important properties of interest are the static and time-dependent correlation functions. These properties are experimentally accessible by performing light-scattering, x-ray scattering, or neutron-scattering experiments. In the limit of zero scattering angle, the scattered intensity becomes proportional to the compressibility, while the correlation length ξ can be determined from the variation of the scattered intensity with the scattering angle (Fisher, 1964). The spectrum of the scattered light yields the decay rate of the fluctuations (Swinney and Henry, 1973). By measuring the scattered light as a function of height near the critical point, one can determine these properties as a function of chemical potential (Alekhin *et al.*, 1969; Chalyi and Alekhin, 1971; Kim *et al.*, 1974; Lakoza *et al.*, 1974; Cannell, 1975).

In order to assess the resolution obtainable in scattering experiments, two effects need to be considered, namely limitations due to the gravitationally induced inhomogeneity and problems caused by multiple scattering. In this section we present some simple estimates of the conditions where both these effects will become important.

Gravity imposes limitations when the structure factor begins to vary over the height of the scattering volume. For x-ray scattering measurements in argon the effect has been discussed by Dobbs and Schmidt (1973). Here we consider the conditions normally encountered in light-scattering experiments.

The effects of gravity on the interpretation of light-scattering measurements have been the subject of a number of papers by Miller *et al.* (Splittorf and Miller, 1974; Leung and Miller, 1975, 1977a, 1977b). They consider an optical arrangement in which the light beam passes through the sample in the vertical direction. In this arrangement, only the scattered beam is subject to the bending effects discussed earlier. Actual light-scattering experiments thus far reported have been conducted with a horizontal light beam. A detailed analysis of the gravity effects in such conventional light-scattering experiments was recently made by Cannell (1977b).

The magnitude of gravity effects on light-scattering measurements will depend on the scattering angle (Cannell, 1977b). However, in practice one wants to know the scattering function over a large range of wave numbers including those corresponding to small scattering angles. Therefore, as a simple rule to assess whether or not scattering experiments are free from gravitationally induced averaging errors, we require that the compressibility not vary significantly over the height of the scattering volume. That is, the conditions are again given by Eqs. (4.10)–(4.14) in Sec. IV B, where h is now the height of the scattering volume. In light-scattering experiments one can use a weakly focused beam with a diameter of about 100μm. Estimates for the gravitationally affected range in xenon with $h = 100\mu\text{m}$ are given in the last column of Table V. We conclude that in earth-bound experiments the effects become severe at temperatures of the order of $\Delta T^* \simeq 10^{-5}$ which are of the same order as the limitations due to beam bending. The resolution is not significantly improved by using scattering volumes with smaller heights. First, stronger focusing would require much lower power levels than currently used, so as to avoid local heating. Stronger focusing would also increase the angular spread of the scattered light collected by the detector. Finally, the experiments would still be subject to the limitations due to beam bending summarized in Table VII.

The width of the Rayleigh line in the spectrum of the scattered light is proportional to the decay rate of the fluctuations of the order parameter. In the hydrodynamic regime where the wavelength of the fluctuations is larger than the correlation length, this decay is determined by the thermal diffusivity which varies as ξ^{-1}. In order to guarantee that the measurement of *any* property that is directly related to the correlation length be not affected by gravitational averaging errors, we require

$$\left|\xi\left(z+\frac{h}{2}\right)-\xi\left(z-\frac{h}{2}\right)\right| \leqslant p\,\xi(z)\,. \qquad (5.14)$$

In analogy to the derivation of Eqs. (4.11) and (4.13) from (4.8), this condition implies

$$|\Delta\rho^*| \geqslant |\Delta\rho^*_{\min}| = \left(\frac{g^*h}{pH_0D}\,\frac{\nu}{\beta\delta}\right)^{1/\delta}, \qquad (T=T_c)\,, \quad (5.15)$$

$$\Delta T^* \geqslant \Delta T^*_{\min} = \left[\frac{g^*h}{H_0}\,\frac{b}{a}\left(\frac{\nu-0.16/b^2}{p}\right)^{1/2}\right]^{1/\beta\delta}, \qquad (\rho=\rho_c)\,. \quad (5.16)$$

In particular, for xenon

$$|\Delta\rho^*| \geqslant |\Delta\rho^*_{\min}| = 0.15\left(\frac{g^*h}{p}\right)^{0.21}, \qquad (T=T_c)\,, \quad (5.17a)$$

$$\Delta T^* \geqslant \Delta T^*_{\min} = 2.7\times10^{-3}\left(\frac{g^*h}{\sqrt{p}}\right)^{0.64}, \qquad (\rho=\rho_c)\,. \quad (5.17b)$$

The region around the critical point where correlation length measurements are affected by gravitational averaging errors is very similar to the corresponding range for compressibility measurements [cf. Eq. (4.14)].

The turbidity of the sample is equal to the total scattering intensity integrated over all scattering angles. The turbidity can be determined experimentally by measuring the intensity of the transmitted beam relative to the intensity of the incident beam. Assuming a simple form for the correlation function, turbidity measurements have been used to determine the correlation length as a function of temperature (Puglielli and Ford, 1970; Balzarini and Ohrn, 1972; Cannell, 1975). When such measurements are conducted with the fluid in thermodynamic equilibrium, the limitations are indeed determined by the gravitational averaging errors discussed above. However, multiple scattering and attenuation of the scattered beam lead to several additional complications in the interpretation of intensity measurements of light scattered at finite scattering angles.

The effects of double scattering on the scattered intensity have been considered by a number of investigators (Chalyi, 1969; Oxtoby and Gelbart, 1974a, 1974b; Reith and Swinney, 1975; Bray and Chang, 1975; Boots *et al.*, 1976; Holm, 1977). Recently increased attention has also been paid to the effect of double scattering on the spectral distribution of scattered light (Beysens *et al.*, 1976; Beysens and Zalczer, 1977; Sorensen *et al.*, 1977). In practice, most fluids become so opaque near the gas-liquid critical point that triple and higher-order scattering cannot be neglected (Trappeniers *et al.*, 1977).

When the wavelength λ of the incident light is significantly larger than the correlation length, the turbidity τ may be approximated by (Puglielli and Ford, 1970)

$$\tau \simeq \frac{8\pi^3}{3\lambda^4}\left(\frac{\partial n}{\partial\rho}\right)_T^2 k_BT\chi_T\,. \qquad (5.18)$$

Corrections due to turbidity become severe for an optical path length w, such that $\tau w \geqslant 1$. Under approximately the same conditions, corrections due to multiply scattered light reaching the detector also become severe. Thus to ensure that these corrections are small, we require

$$w\tau = w\tau_0\chi_T^* \leqslant 1\,, \qquad (5.19)$$

where

$$\tau_0 \simeq \frac{8\pi^3}{3\lambda^4}\,\frac{k_BT_c}{P_c}\,4n_c^2n_c'^2\,. \qquad (5.20)$$

This condition implies

$$r \geqslant (w\tau_0\Gamma)^{1/\gamma}\,. \qquad (5.21)$$

In particular, at the critical density and temperature,

$$\Delta T^* \geqslant \Delta T^*_{\min} = (w\tau_0\Gamma)^{1/\gamma}\,, \qquad (\rho=\rho_c)\,, \quad (5.22a)$$

$$|\Delta\rho^*| \geqslant |\Delta\rho^*_{\min}| = \left(w\tau_0\,\frac{1}{\delta D}\right)^{\beta/\gamma}, \qquad (T=T_c)\,. \quad (5.22b)$$

For xenon we obtain

$$\Delta T^* \geqslant \Delta T^*_{\min} = \left(3.4\times10^{-29}\frac{w}{\lambda^4}\right)^{0.81}, \qquad (\rho=\rho_c)\,, \quad (5.23a)$$

$$|\Delta\rho^*| \geqslant |\Delta\rho^*_{\min}| = \left(1.6\times10^{-29}\frac{w}{\lambda^4}\right)^{0.26}, \qquad (T=T_c)\,, \quad (5.23b)$$

where the path length w and the wavelength λ are to be expressed in meters. For light-scattering measurements at the wavelength $\lambda = 0.6328\,\mu$m of a He–Ne laser and a typical optical cell with a width $w = 1$cm, Eq. (5.23a) implies $\Delta T^* \geqslant 1.7\times10^{-4}$. A comparison with the information in the third column of Table V confirms that under normal circumstances the restrictions on light-scattering experiments due to turbidity are more severe than those due to gravitational averaging errors, as was also emphasized by Cannell (1977b).

In order to benefit from light-scattering experiments in a low-gravity environment, it is imperative that the effects of turbidity be reduced significantly. For this purpose one may consider three options. The first option is to reduce the width w of the optical cell. Typical optical cells have a width of 10mm, while more specialized cells have been made with a width of the order of 1mm. It may perhaps be possible to work with cells with a width of 0.1mm, although one then must discriminate against scattering from surface layers and the inner cell walls. A second option is to choose a fluid with a smaller refractive index. In binary liquids near the critical point of mixing, turbidity and multiple scattering can be reduced drastically by selecting a mixture of liquids with closely matched refractive indices (Chang *et al.*, 1976). For light-scattering experiments near the gas-liquid critical point the freedom of choice is much more restricted. Nevertheless, since the turbidity is proportional to $4n_c^2n_c'^2 \simeq (n_c^2-1)^2$, we note from the information provided in Tables II and III that the turbidity of ^{3}He or ^{4}He near the gas-liquid critical point would be about 100 times smaller than that of xenon. Since the turbidity is inversely proportional to λ^4, the third and most promising option is to conduct scattering experiments at longer wavelengths. Small continuous He–Ne lasers yielding wavelengths at $1.152\,\mu$m and $3.391\,\mu$m do exist. Photomultipliers still work at a wavelength of about $1\,\mu$m so that one still could conduct spectral measurements as well as intensity measurements. At a wavelength of $3\,\mu$m the use of

TABLE IX. Range of temperatures and densities around the critical point of xenon where light-scattering experiments are severly affected by attenuation and multiple scattering.

	$w=10^{-2}$m		$w=10^{-3}$m		$w=10^{-4}$m	
	$\rho=\rho_c$ $\Delta T^*_{\min}$	$T=T_c$ $\Delta\rho^*_{\min}$	$\rho=\rho_c$ $\Delta T^*_{\min}$	$T=T_c$ $\Delta\rho^*_{\min}$	$\rho=\rho_c$ $\Delta T^*_{\min}$	$T=T_c$ $\Delta\rho^*_{\min}$
$\lambda=0.633$ μm	1.7×10^{-4}	4.9×10^{-2}	2.6×10^{-5}	2.7×10^{-2}	4.1×10^{-6}	1.5×10^{-2}
$\lambda=1.152$ μm	2.4×10^{-5}	2.6×10^{-2}	3.8×10^{-6}	1.4×10^{-2}	5.9×10^{-7}	7.7×10^{-3}
$\lambda=3.391$ μm	7.5×10^{-7}	8.4×10^{-3}	1.2×10^{-7}	4.6×10^{-3}	1.8×10^{-8}	2.5×10^{-3}

photoconductive detectors would be required, and the choice of window materials would become more restricted. In Table IX we present a summary of the range of temperatures and densities around the critical point of xenon, where light-scattering experiments are severely affected by turbidity for various widths of the optical cell and wavelengths of the incident beam. In order to judge the feasibility of increasing the experimental range accessible with light scattering in a low gravity environment, the data in Table IX should be compared with the information provided in the third column of Table V.

VI. ATTEMPTS TO SUPPRESS DENSITY GRADIENTS INDUCED BY THE EARTH'S GRAVITATIONAL FIELD

The fundamental effect of gravity is to induce a spatially inhomogeneous chemical potential in the fluid. In order to cope with this effect, one can consider three different kinds of strategies. The first approach is to perform the experiments which probe the fluid over a smaller range of heights. The resolution to be obtained in this approach was discussed in the preceding sections. A second possible strategy is to offset the gravitational contribution to the chemical potential with a contribution to the chemical potential from another field, such as an electrostatic field. We shall comment on this option at the end of this section. A third strategy is to bring the system into a suitable nonequilibrium state in which the equilibrium gradients have not developed. This strategy is the one commonly used in studying binary liquid mixtures near the consolute point. In such experiments one usually investigates fluid mixtures which have been stirred. Such samples have a nearly uniform density, temperature, and composition. If the binary mixture is left undisturbed, it will approach true thermodynamic equilibrium; this approach is effected by diffusion and sedimentation leading to a stratification of the composition in the earth's gravitational field (Greer *et al.*, 1975; Block *et al.*, 1977). In the case of binary mixtures in containers that are centimeters high, this relaxation takes weeks or months; hence, it is rarely allowed to go to completion (Giglio and Vendramini, 1978; Knobler and Scott, 1978). In this section we investigate to what extent gravity effects near the gas-liquid critical point can be suppressed by not allowing the system to approach thermodynamic equilibrium. In particular we consider the possibilities of imposing a stationary temperature gradient, quenching the system, or stirring the system.

Near the gas-liquid critical point the isobaric thermal expansion coefficient $\alpha_p=-\rho^{-1}(\partial\rho/\partial T)_p$ diverges as strongly as the compressibility. This divergence causes the density gradients to be strongly affected by the pressure of small temperature gradients (Berestov and Malyshenko, 1970; While and Maccabee, 1975). Conceptually, this phenomenon could be used to advantage by imposing a temperature gradient with the purpose of compensating for the gravitationally induced density gradient. Imagine a fluid layer confined between two horizontal parallel plates in which a spatially uniform temperature gradient is established by heating the layer from the bottom and cooling it from the top. If the temperature gradient dT/dz is chosen such that

$$\frac{dT}{dz}=-\rho g\left(\frac{\partial T}{\partial P}\right)_\rho , \tag{6.1}$$

the fluid density in hydrostatic equilibrium will be independent of height to an excellent approximation. This is true even very close to the critical point, because $(\partial T/\partial P)_\rho$ approaches a finite constant at the critical point. The required gradient may be estimated from the rule of thumb

$$\left(\frac{\partial T}{\partial P}\right)_\rho \approx \frac{T_c}{6P_c} . \tag{6.2}$$

In the presence of such a temperature gradient, an experimental probe which averages over a finite range of heights will now sample a range of temperatures instead of a range of densities. For xenon a temperature gradient of the order of 0.1 K/m is needed to attain a constant density. Thus a 100μm wide probe, such as the laser beam considered in Sec. V.B, would sample a range of $\Delta T\approx10^{-5}$ K in temperature. From Eq. (6.1) it follows that the required temperature gradient scales linearly with g^*.

When the experiments are performed in the presence of a temperature gradient, the system is not in thermodynamic equilibrium. Nevertheless, it is customarily assumed that such measurements yield averages over local equilibrium states provided that the gradient is sufficiently small so that the local fluid properties do not vary significantly across a distance of a correlation length. This assumption has been made explicitly or implicitly in the interpretation of almost all experiments near consolute points in binary liquid mixtures, where the effects of the diffusion flux on the measurements is assumed to be negligible. One may consider this assumption to be confirmed in part by the experimental result that the critical exponents in binary liquid mixtures are the same as those measured in pure fluids near the gas-liquid critical point (Greer, 1978). Thus we may assume that the effects of the stationary heat flux on the measurements are negligible as well.

Near the critical point the tendency for temperature gradients to generate convection becomes large (Michels and Sengers, 1962). Hence we need to investigate whether in practice a stationary temperature gradient can be imposed while still maintaining hydrostatic equilibrium. The equations governing the onset of convection in fluids near the critical point have been recently reviewed by Gitterman (1978). For our purpose a simplified discussion will suffice.

Away from the critical point, where the compressibility is small, the onset of convection is determined by the value of the Rayleigh number N_R. In a horizontal fluid layer heated from below, convection will occur if the Rayleigh number exceeds a critical value. This critical value depends on the actual boundary conditions (Pellew and Southwell, 1940). For an infinite horizontal fluid layer of height h enclosed between two rigid horizontal plates the critical Rayleigh number is 1708. In order to apply this criterion in the critical region, where the compressibility is large, we replace the Rayleigh number N_R by the modified Rayleigh number $\bar{N}_R$, defined as (Normand *et al.*, 1977; Gitterman, 1978)

$$\bar{N}_R = -\left(\frac{dT_e}{dz}\right)\frac{g\alpha_p h^4}{D_\eta D_T}\,. \tag{6.3}$$

Here D_T is the thermal diffusivity and D_η the viscous diffusivity, which is the shear viscosity η divided by the density ρ. The modified Rayleigh number $\bar{N}_R$ includes the factor dT_e/dz rather than the actual temperature gradient dT/dz; dT_e/dz is the amount by which the actual temperature gradient exceeds the adiabatic gradient $\rho g(\partial T/\partial P)_S$, i.e., (Gitterman, 1978),

$$-\frac{dT_e}{dz} = -\frac{dT}{dz} - \rho g\left(\frac{\partial T}{\partial P}\right)_S \tag{6.4}$$

(In this paper the coordinate z is taken to increase in the direction opposite to the gravitational field, so that dT/dz is negative). We note that

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial T}{\partial P}\right)_\rho \left[1-\frac{C_v}{C_p}\right]. \tag{6.5}$$

The specific heat ratio C_v/C_p is very small throughout the region of interest, since it varies as $r^{\gamma-\alpha} \approx r^{1.1}$. Thus the limit $dT_e/dz \to 0$ corresponds to the limit of uniform density in which the driving force for convection has disappeared.

The dependence of the Rayleigh number on ΔT^* and $\Delta\rho^*$ in the critical region has been investigated earlier; for given instrumental conditions, this quantity increases rapidly when the critical point is approached (Michels and Sengers, 1962). The product $D_\eta D_T$ vanishes as the inverse correlation length (Hohenberg and Halperin, 1977). Thus, at the critical density, the Rayleigh number diverges as

$$\frac{\bar{N}_R}{(-dT_e/dz)g^*h^4} = N_0(\Delta T^*)^{-(\gamma+\nu)}. \tag{6.6}$$

For xenon we find

$$\frac{\bar{N}_R}{(-dT_e/dz)g^*h^4} \simeq 1\times 10^{13}(\Delta T^*)^{-1.87}\,\mathrm{m}^{-3}\mathrm{K}^{-1}. \tag{6.7}$$

As mentioned above, if $g^* = 1$, the adiabatic gradient is about 10^{-3} K/cm. Thus in a fluid layer, 1cm high, whose top is at the critical temperature T_c, ΔT^* is less than 0.3×10^{-5} everywhere in the sample. In order for the Rayleigh number $\bar{N}_R$ to be smaller than 1700, the temperature gradient $-dT_e/dz$ must be smaller than 10^{-14} K/cm. We conclude that in practice convection cannot be avoided when a temperature gradient close to the adiabatic temperature gradient is imposed. Furthermore, Shteinberg (1971) has argued that in a uniform fluid layer heated from below, an oscillatory instability may occur, even when a temperature gradient smaller than the adiabatic gradient is imposed. Because of the difficulty of avoiding convection, we conclude that suppression of the density gradient by imposing a stationary temperature gradient is not a realistic option.

An alternate procedure is to stir the fluid sample either by inducing convection currents (Cannell, 1975) or by using a mechanical stirrer (Voronel, 1976). After the sample has been stirred, it will first approach mechanical equilibrium via relaxation of the sound modes and viscous modes. Since the sound absorption coefficient becomes very large, this process is determined by the viscous relaxation time

$$\tau_\eta = l^2/\pi^2 D_\eta\,, \tag{6.8}$$

where l is the distance in the fluid to the nearest wall. The shear viscosity is weakly divergent (Hohenberg and Halperin, 1977), and the viscous relaxation time is of the same order of magnitude as outside the critical region; in practical experimental situations this time is of the order of a minute. On the other hand, the approach to thermal equilibrium is determined by the thermal relaxation time (Levelt Sengers, 1975)

$$\tau_T = l^2/\pi^2 D_T\,, \tag{6.9}$$

which diverges as (Hohenberg and Halperin, 1977) $\tau_T \simeq 6l^2\eta\xi/\pi k_B T_c$. At $|\Delta T^*| < 10^{-4}$ this relaxation time becomes of the order of hours. Hence, after the sample has been stirred, the sound and viscous modes relax in a time interval during which the relaxation of thermal energy is negligibly small. Thus the entropy remains uniform and the adiabatic gradient is established in the system. As noted earlier from Eq. (6.5), near the critical point this adiabatic gradient corresponds to a constant density profile. During the subsequent stage the adiabatic profile will slowly relax to the isothermal profile. This is precisely what was observed optically by Cannell (1975) when he heated sulfur hexafluoride at the critical density and then rapidly cooled the system to $T_c + 0.012$K. More recently, Hayes and Carr (1977) used a quenching technique to study the coexistence curve of xenon near the critical point. They rapidly cooled samples in glass containers through the critical temperature. The fluid separates into coexisting phases throughout the sample volume. The liquid droplets fall and the vapor bubbles rise adiabatically. This counterflow produces a turbulent mixing. The measurements of Hayes and Carr were completed before the isothermal state could be established by heat conduction.

It is also possible to induce the adiabatic gradient by stirring the sample mechanically and then waiting for the fluid motion to subside. This situation may have been approached in the pioneering specific heat measurements of (Voronel, 1976). Their calorimeter consisted of a poorly conducting, thin walled shell enclosing a sample of substantial height (10cm), which was stirred at intervals of a fraction of a minute. (In contrast to Voronel, other experimenters have attempted to achieve isothermal density versus height profiles in calorimeters by using samples of small height contained in heavy highly conducting walls.) In practice, Voronel, *et al.* found the experimental results becoming dependent on the stirring frequency at $|\Delta T^*| < 10^{-4}$. The stirring interval used was probably somewhat shorter than the viscous relaxation time of the samples, so that the adiabatic density versus height profile was not fully established.

Assuming that the experiments are concluded before the adiabatic gradient relaxes, the resolution is still limited, since the local properties of the fluid are now probed over a finite range of temperatures. The limits of resolution can be estimated by requiring an analogy to (4.2),

$$|Q(\rho, T(z+\frac{h}{2})) - Q(\rho, T(z-\frac{h}{2}))| \leqslant p Q(\rho, T(z)) . \quad (6.10)$$

Estimating the temperature gradient from Eqs. (6.1) and (6.2), this condition implies

$$\frac{\rho^* g^* h}{6H_0}\left|\left(\frac{\partial Q}{\partial T^*}\right)_\rho\right| \leqslant pQ . \quad (6.11)$$

Assuming that the quantity Q diverges as $Q_0|\Delta T^*|^{-\phi}$, we find at the critical density

$$\Delta T^* \geqslant \Delta T^*_{\text{min}} = \frac{g^* h}{6H_0}\,\frac{\phi}{p} , \qquad (\rho = \rho_c) . \quad (6.12)$$

For xenon we thus obtain

$$\Delta T^* \geqslant \Delta T^*_{\text{min}} = 3\times 10^{-4} g^* h \frac{\phi}{p} , \qquad (\rho = \rho_c) . \quad (6.13)$$

Using a hypothetical $100\,\mu$m wide laser beam for measuring the correlation length ($\phi = \nu$) and requiring a precision of one percent, one can in principle approach the critical point up to $\Delta T^*_{\text{min}} = 2\times 10^{-6} g^*$. If the same experiment were conducted in thermodynamic equilibrium, it follows from Eq. (5.17b) that the resolution would be limited by $\Delta T^*_{\text{min}} = 3\times 10^{-5} g^{*0.64}$. Hence experiments in the presence of the adiabatic gradient do allow us to approach the critical point more closely than experiments in the presence of the isothermal profile. Indeed, Cannell (1975) has exploited this feature of the adiabatic temperature profile to measure the turbidity of SF_6 down to $\Delta T^* = 4\times 10^{-6}$. Because the adiabatic temperature profile suppresses the density gradient, the beam-bending effects discussed in Sec. V A do not cause problems in this method.

We emphasize that the closest possible approach to the critical point ΔT^*_{min} in an isothermal experiment scales as $g^{*0.64}$, while it scales as g^* in an adiabatic experiment. Thus the relative advantage of stirring becomes even more pronounced at reduced gravitational levels.

As mentioned in the beginning of this section, the gravitational contribution to the chemical potential could in principle be compensated by a contribution from an electrostatic field. This would require an electric field whose strength E varies with the square root of the height (Landau and Lifshitz, 1960; Debye and Kleboth, 1965; Voronel and Gitterman, 1969),

$$gz = \tfrac{1}{2}E^2(\partial \varepsilon/\partial \rho)_T , \quad (6.14)$$

where ε is the (absolute) dielectric constant. For xenon the electric field would have to vary as $9\times 10^7\sqrt{z}$ V/m where the vertical coordinate z is expressed in meters. To our knowledge, an electrode configuration that produces the desired field throughout a macroscopic volume has not been designed. Moreover, the fact that an inhomogeneous field is required leads to additional complications. Since an electric field affects the location of the critical point (Landau and Lifshitz, 1960), the critical temperature, and hence ΔT^*_{min} would vary with the position in the fluid in a way which is difficult to estimate at present (Voronel and Gitterman, 1969).

VII. INTRINSIC GRAVITY EFFECTS

In the preceding sections we discussed the limitations in various experimental methods near the critical point of a fluid resulting from averaging the local thermodynamic properties over a finite height. In addition, earth-bound experiments sufficiently close to the critical point are subject to intrinsic limitations due to the fact that the gravitational field modifies the local fluid properties themselves and changes the nature of the transition. If the system were homogeneous and in true thermodynamic equilibrium, the compressibility and, hence, the correlation length would actually diverge at the critical point. However, the presence of the gravitational field prevents the fluctuations from growing indefinitely and the compressibility will, in fact, remain finite.

The assumption that the local thermodynamic properties may be identified with those of a homogeneous system with the same temperature and the same uniform density in the thermodynamic limit is justified when the fluid is locally homogeneous over distances of the order of the correlation length. The complications that arise when the macroscopic thermodynamic relations can no longer be applied at the local level will be referred to as nonlocal effects. Such effects will enter when the correlation length ξ calculated in the thermodynamic limit starts to vary over its own height $h = \xi$. It thus follows that for measurements conducted with a precision p, nonlocal effects can be neglected as long as

$$\Delta\xi = |\xi(z+\frac{\xi}{2}) - \xi(z-\frac{\xi}{2})| \leqslant p\xi(z) . \quad (7.1)$$

For densities not too close to the critical density we approximate Eq. (7.1) by

$$\left|\left(\frac{\partial \xi}{\partial z}\right)_T\right| = \frac{g^*}{H_0}\chi^*_T\left|\left(\frac{\partial \xi}{\partial \rho^*}\right)_T\right| \leqslant p \quad (7.2)$$

so that

$$r \geqslant r_{\min} = \left(\frac{g^*\xi_0}{H_0 a p}\right)^{1/(\gamma+\beta\delta)} \left|\frac{2b^2\nu\theta R(\theta) - (1-b^2\theta^2)R'(\theta)}{q(\theta)}\right|^{1/(\nu+\beta\delta)} \tag{7.3}$$

It follows that at the critical temperature

$$|\Delta\rho^*| \geqslant |\Delta\rho^*_{\min}| = \left[\frac{g^*\xi_0}{H_0 p D}\frac{\nu}{\beta\delta}\left(\frac{1}{\Gamma D\delta}\right)^{\nu/\gamma}\left(1+\frac{0.16}{b^2}\right)\right]^{\beta/(\nu+\beta\delta)}, \quad (T=T_c)\,. \tag{7.4a}$$

Near the critical density, condition (7.2) becomes unrealistic because of the rapid variation of $\partial\xi/\partial z$ and we return to the integrated form (7.1). The distance Δz_p over which the correlation length changes by a fraction p can be readily evaluated in analogy with Eq. (4.12). This distance should be larger than $\xi \simeq \xi_0(\Delta T^*)^{-\nu}$, and we obtain the estimate

$$\Delta T^* \geqslant \Delta T^*_{\min} = \left[\frac{g^*\xi_0}{H_0}\frac{b}{a}\left(\frac{\nu - 0.16/b^2}{p}\right)^{1/2}\right]^{1/(\nu+\beta\delta)}, \quad (\rho=\rho_c)\,. \tag{7.4b}$$

For xenon these estimates become

$$|\Delta\rho^*| \geqslant |\Delta\rho^*_{\min}| = 8.9\times10^{-3}(g^*/p)^{0.15}, \quad (T=T_c) \tag{7.5a}$$

$$\Delta T^* \geqslant \Delta T^*_{\min} = 5.5\times10^{-7}(g^*/\sqrt{p})^{0.46}, \quad (\rho=\rho_c)\,. \tag{7.5b}$$

In Fig. 6 we indicate the region of temperatures and densities around the critical point of xenon where the behavior of the fluid is modified by nonlocal effects and, hence, where its properties will be fundamentally different from those of a fluid in the absence of gravity. From Eq. (7.5b) we conclude that in the earth's gravitational field $\Delta T^*_{\min} = 1.6\times10^{-6}$. This value of $\Delta T^*_{\min}$ is easily achieved with existing techniques of temperature control. Thus, if the required spatial resolution could be obtained, nonlocal effects would be measurable in pure fluids on earth. It follows from (7.5) that within this resolution nonlocal effects will be negligible at the gravitational levels accessible in a space laboratory.

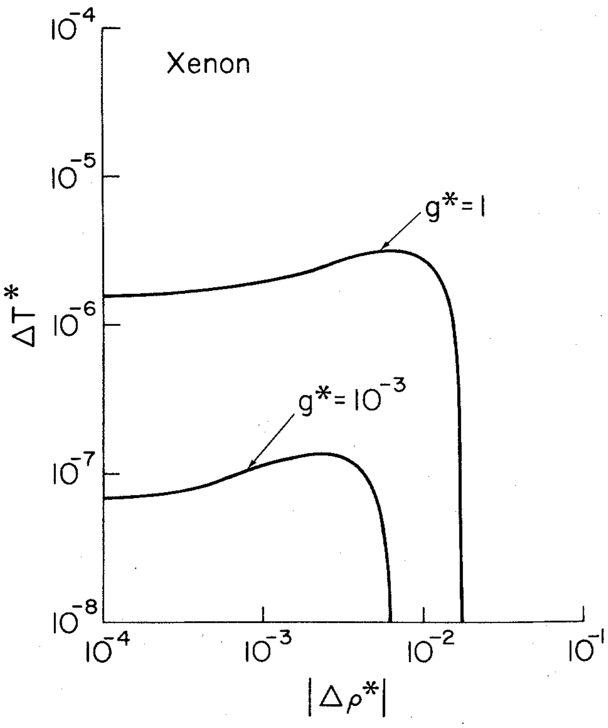

FIG. 6. Range of temperatures and densities around the critical point of xenon for $g^*=1$ and $g^*=10^{-3}$ where the fluid properties are modified by nonlocal effects.

When the condition (7.1) is violated, further increase in the range of the fluctuations will be suppressed by nonlocal effects. The maximum correlation length attainable in the vertical direction may be estimated from (7.1) by taking $p \approx 1$. Hence we conclude from Eq. (7.5b) for xenon at $\rho=\rho_c$

$$\xi \leqslant \xi_{\max} \simeq 1.7\times10^{-6}g^{*-0.29}\,\mathrm{m}. \tag{7.6}$$

In earth-bound experiments the correlation length in the vertical direction cannot grow beyond 1.7×10^{-6} m. When the gravity is reduced, the maximum attainable correlation length will grow inversely proportional to $g^{*0.3}$.

We can expect that any external field will modify the thermodynamic properties of a system near a critical point, when the nature of the fluctuations in the presence of the field becomes significantly different from the fluctuations in the absence of that field. If the external field contribution to the potential energy associated with a "typical" fluctuation becomes a fraction p of the thermal energy k_BT, we expect that the fluctuations will be suppressed by the external field.

We can thus formulate an alternate criterion for the suppression of the vertical component of the density fluctuations in a fluid in a gravitational field by considering the gravitational potential energy of a fluctuation. The mean square fluctuations of the number of molecules N in a volume V is given by (Landau and Lifshitz, 1958)

$$\langle(\Delta N)^2\rangle = k_BTV\chi_T/m^2\,, \tag{7.7}$$

where m is the molecular mass. Thus the gravitational potential energy of a "typical" fluctuation with volume ξ^3 is of the order of $mg\xi\sqrt{\langle(\Delta N)^2\rangle}$. We thus expect nonlocal effects to be absent provided that

$$mg\xi(\langle(\Delta N)^2\rangle)^{1/2} \leqslant pk_BT\,, \tag{7.8}$$

which, together with Eq. (7.7), implies

$$\frac{g^*}{H_0 p}\left(\frac{P_c}{k_BT}\xi^5\chi^*_T\right)^{1/2} \leqslant 1\,. \tag{7.9}$$

At the critical density $\rho=\rho_c$ we thus obtain

$$\Delta T^* \geqslant \Delta T^*_{\min} = \left(\frac{g^*}{H_0 p}(\xi_0^5\Gamma P_c/k_BT)^{1/2}\right)^{2/(\gamma+5\nu)}, \quad (\rho=\rho_c)\,. \tag{7.10}$$

In particular, for xenon

$$\Delta T^* \geqslant \Delta T^*_{\min} = 3.9\times10^{-7}(g^*/p)^{0.46}, \quad (\rho=\rho_c)\,. \tag{7.11}$$

This estimate is of the same order of magnitude as earlier obtained in Eq. (7.5b).

TABLE X. Limitation of experiments near the gas-liquid critical point.[a]

Experiment	Measured property	Characteristic length	Nature of limitation	Excluded range on earth $\rho=\rho_c$ $\Delta T^*_{\min}$	Excluded range on earth $T=T_c$ $\Delta\rho^*_{\min}$	Excluded range at $10^{-3}g_0$ $\rho=\rho_c$ $\Delta T^*_{\min}$	Excluded range at $10^{-3}g_0$ $T=T_c$ $\Delta\rho^*_{\min}$	Excluded range at $10^{-6}g_0$ $\rho=\rho_c$ $\Delta T^*_{\min}$	Excluded range at $10^{-6}g_0$ $T=T_c$ $\Delta\rho^*_{\min}$
PVT	Density	Cell 1cm high	Density gradient	6×10^{-4}	8×10^{-2}	2×10^{-6}	1×10^{-2}	1×10^{-8}	2×10^{-3}
PVT	Compressibility	Cell 1cm high	Compressibility gradient	8×10^{-4}	2×10^{-1}	1×10^{-5}	4×10^{-2}	1×10^{-7}	1×10^{-2}
Capicitance	Density	Spacing between plates 0.2 mm	Density gradient	3×10^{-5}	3×10^{-2}	1×10^{-7}	4×10^{-3}	4×10^{-10}	7×10^{-4}
Capicitance	Compressibility	Spacing between plates 0.2 mm	Compressibility gradient	7×10^{-5}	8×10^{-2}	8×10^{-7}	2×10^{-2}	1×10^{-8}	4×10^{-3}
Calorimetry	Heat capacity	Cell 1cm high	Rearrangement of profile	3×10^{-4}	1×10^{-1}	4×10^{-6}	3×10^{-2}	5×10^{-8}	7×10^{-3}
Refractive index	Compressibility	Path in cell 3 mm	Beam bending	2×10^{-5}	4×10^{-2}	2×10^{-7}	8×10^{-3}	1×10^{-9}	2×10^{-3}
Light scattering ($\lambda=0.633\mu$m)	Correlation function	Path in cell 3 mm	Turbidity	6×10^{-5}	3×10^{-2}	6×10^{-5}	3×10^{-2}	6×10^{-5}	3×10^{-2}
Light scattering ($\lambda=1.152\mu$m)	Correlation function	Path in cell 3 mm	Turbidity	9×10^{-6}	2×10^{-2}	9×10^{-6}	2×10^{-2}	9×10^{-6}	2×10^{-2}
Light scattering	Correlation length	Height of scattering volume 0.1 mm	Correlation length gradient	3×10^{-5}	6×10^{-2}	4×10^{-7}	1×10^{-2}	5×10^{-9}	3×10^{-3}
All	Any	Correlation length	Nonlocal effects	2×10^{-6}	2×10^{-2}	7×10^{-8}	6×10^{-3}	3×10^{-9}	2×10^{-3}

[a] The estimates refer to xenon when the indicated property is to be measured within 1%.

The dependence of $\Delta T^*_{\min}$ on the magnitude of the gravitational field g has also been investigated by Malyshenko and Mika (1974). They concluded that $\Delta T^*_{\min}$ scales as $g^{*4/7\gamma} \simeq g^{*0.46}$ in agreement with our result. Below the critical temperature the thickness of the interface between vapor and liquid is proportional to the correlation length (Widom, 1972). Thus in the absence of a gravitational field one would expect the interface thickness to grow indefinitely upon approaching the critical point. In the presence of a gravitational field the interface thickness will not grow beyond a size estimated by Eq. (7.6). Due to nonlocal effects, the temperature of meniscus disappearance in a gravitational field can no longer be identified with the thermodynamic critical temperature of the hypothetically homogeneous fluid (Malyshenko and Mika, 1974).

The gravity effects may be enhanced by performing critical phenomena experiments in a centrifuge (Block *et al.*, 1977; Alder *et al.*, 1978). However, in that case the interpretation of the experiment depends on the distance R of the cylindrical fluid layer from the axis of rotation. If this distance R is substantially larger than the correlation length, the above formulae still apply provided that g is replaced with $\omega^2 R$, where ω is the frequency of rotation (Malyshenko and Mika, 1974). Otherwise, the analysis is complicated by the inhomogeneous character of the induced effective gravitational field (Alder *et al.*, 1978).

VIII. DISCUSSION

As a summary we present in Table X for a variety of experiments in xenon estimates of temperatures and densities near the critical point where the measurements become affected by gravitationally induced averaging errors. From the information provided in this paper similar tables can be readily prepared for a large number of fluids.

For measurements with a precision of the order of one percent, the range of true asymptotic critical behavior is expected to be of the order of $r \approx \Delta T^* \simeq 10^{-4}$. Fluid properties that require experimental probes with heights of the order of millimeters cannot be measured accurately in this range without averaging errors due to the presence of the earth's gravitational field. With optical techniques some properties such as the equation of state can be measured in a range that approaches the critical point at most one decade beyond 10^{-4}. It appears very difficult to measure in earth-bound experiments near the gas-liquid critical point fluid properties in a range closer than 10^{-5} without serious gravity effects. The data in Table X indicate to what extent these restrictions are reduced at the gravitational levels accessible in a space laboratory.

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