International Journal of Thermophysics, Vol. 6, No. 6, 1985

Critical Phenomena in Gases in the Presence of Gravity[1]

J. V. Sengers[2] and J. M. J. van Leeuwen[3]

Gravity induces an inhomogeneous density distribution in fluids near the gas–liquid critical point. In first approximation the local properties of the fluid at a given height can be identified with those of a homogeneous system with the same temperature and density. Very close to the critical point the density gradients become so steep that gravity affects the local properties of the fluid directly. A survey is presented of the nature and magnitude of these intrinsic gravity effects.

KEY WORDS: compressibility; correlation length; critical phenomena; density profiles; gravity effects; interface thickness; surface tension.

1. INTRODUCTION

The presence of the earth's gravitational field has generally a negligible effect on the thermophysical properties of fluids. A notable exception, however, is a gas near its critical point. Here gravity induces an inhomogeneous density distribution and all thermophysical properties will vary as a function of height. In order to account for these effects in critical-phenomena experiments, one usually assumes that at a given level the local properties of the fluid can still be identified with those of a locally homogeneous fluid [1, 2]. Very close to the critical point this assumption ceases to be valid due to the interactions between layers of different density. As a consequence, gravity modifies the local fluid properties themselves

[1] Invited paper presented at the Ninth Symposium on Thermophysical Properties, June 24–27, 1985, Boulder, Colorado, U.S.A.

[2] Institute for Physical Science and Technology, University of Maryland, College Park, Maryland 20742, U.S.A.

[3] Laboratorium voor Technische Natuurkunde, Technische Hogeschool Delft, 2600 GA Delft, The Netherlands.

very close to the critical point and changes the nature of the critical-point phase transition. It is the purpose of this paper to give a qualitative and quantitative assessment of these intrinsic gravity effects.

The state of a system near a critical point is characterized by the presence of large fluctuations which lead to a singular behavior of the thermophysical properties. In the modern theory of critical phenomena the effect of these fluctuations is accounted for by a renormalization-group analysis of a system represented by a Landau-Ginzburg Hamiltonian [3]. In order to develop a theory of the gravity effects, one should extend the theory to a renormalization analysis in the presence of an external field. Such an analysis is not yet available. Instead we adopt an approximate procedure in which the effect of the critical fluctuations is incorporated by the adoption of a scaled equation for the free energy and the density profile is determined by minimizing this free energy in the presence of gravity as is done in the squared-gradient theory of van der Waals for the vapor–liquid interface [4]. One then obtains a differential equation for the density ρ as a function of the height z which has the form [5]

$$A\frac{d^2\rho}{dz^2} = \Delta\mu + gz \tag{1}$$

where g is the gravitational acceleration constant. The height z increases in the direction opposite to the gravitational field and the reference level $z = 0$ is chosen at the level where the density ρ equals the critical density ρ_c. The chemical potential difference $\Delta\mu$ is

$$\Delta\mu = \mu(\rho(z), T) - \mu(\rho_c, T) \tag{2}$$

The coefficient A is related to the correlation length ξ and the symmetrized compressibility $\chi = (\partial\rho/\partial\mu)_T$ by

$$A = \xi^2(\rho(z), T)/\chi(\rho(z), T) \tag{3}$$

The quantities $\mu(\rho(z), T)$, $\xi(\rho(z), T)$, and $\chi(\rho(z), T)$ are those of a spatially homogeneous system with uniform density $\rho \equiv \rho(z)$ at the given temperature T. Without the gravitational term gz, Eq. (1) reduces to the differential equation adopted by Fisk and Widom in the theory of the structure of the vapor–liquid interface near the critical point [4, 6]. The squared-gradient theory is approximate since it fails to include in a consistent way the small deviations of the correlation function from the Ornstein–Zernike form [5]. Nevertheless, we expect this procedure to yield a description of the intrinsic gravity effects that is basically correct.

We find it convenient to reduce the thermodynamic functions and variables with the aid of the critical temperature T_c, the critical density ρ_c, and the critical pressure P_c. We thus define

$$T^* = \frac{T}{T_c}, \qquad \rho^* = \frac{\rho}{\rho_c}, \qquad \mu^* = \frac{\mu\rho_c}{P_c} \tag{4}$$

and

$$\Delta T^* = T^* - 1, \qquad \Delta\rho^* = \rho^* - 1, \qquad \Delta\mu^* = \mu^*(\rho(z), T) - \mu^*(\rho_c, T) \tag{5}$$

To facilitate a discussion of the dependence of the gravity effects on g, we also define

$$g^* = \frac{g}{g_0}, \qquad H_0 = \frac{P_c}{\rho_c g_0} \tag{6}$$

where $g_0 = 9.81\ \mathrm{m \cdot s^{-2}}$ corresponds to the earth's gravitational field. Since $\Delta\mu^*$ is an antisymmetric function of $\Delta\rho^*$, it is sufficient to solve the differential equation for $z > 0$ only and we obtain

$$\frac{\xi^2}{\chi^*} \frac{d^2|\Delta\rho^*|}{dz^2} = |\Delta\mu^*| - \frac{g^*}{H_0} z \tag{7}$$

where $\chi^* = (\partial\rho^*/\partial\mu^*)_{T^*} = (\partial\Delta\rho^*/\partial\Delta\mu^*)_{\Delta T^*}$.

2. SCALING LAWS AND UNIVERSALITY IN THE ABSENCE OF GRAVITY

In the absence of gravity the asymptotic critical behavior of the thermodynamic properties can be characterized in terms of scaling laws [7]. For $\Delta\mu^*(\rho, T)$, $\chi^*(\rho, T)$, and $\xi(\rho, T)$ these scaling laws can be written in the form

$$\Delta\mu^* = \pm D|\Delta\rho^*|^{\delta} h(u) \tag{8}$$

$$\chi^{*-1} = D|\Delta\rho^*|^{\gamma/\beta} X(u) \tag{9}$$

$$\xi = \xi_0 R(u)(\chi^*/\Gamma)^{\nu/\gamma} \tag{10}$$

where $u = \Delta T^*/x_0|\Delta\rho^*|^{1/\beta}$ with $x_0 = B^{-1/\beta}$ and $X(u) = \delta(u) - \beta^{-1}u\, dh/du$. The critical exponents β, γ, δ, and ν, which are interrelated by $\gamma = \beta(\delta - 1)$ and $\nu = \beta(\delta + 1)/3$, and the scaling functions $h(u)$ and $R(u)$ are universal, i.e., the same for all systems in a universality class. Fluids near the gas–liquid critical point belong to the universality class of three-dimensional

Table I. Critical-Region Properties for a Number of Fluids[a]

	^3He	SF_6	Xe	Ne	Kr	Ar	N_2	CO_2	Iso-C_4H_{10}	C_2H_4	D_2O	H_2O
P_c (MPa)	0.1168	3.761	5.840	2.730	5.493	4.865	3.398	7.375	3.629	5.040	21.673	22.046
ρ_c ($kg \cdot m^{-3}$)	41.5	730	1110	484	908	535	314	467	226	214	356	323
T_c (K)	3.310	318.69	289.72	44.479	209.29	150.73	126.21	304.13	407.84	282.35	643.89	647.07
x_0	0.940	0.228	0.339	0.340	0.339	0.339	0.302	0.238	0.217	0.260	0.121	0.121
D	11.6	6.1	7.9	8.3	7.9	7.9	8.4	6.4	4.8	5.6	2.07	2.07
Γ	0.139	0.046	0.058	0.055	0.058	0.058	0.047	0.046	0.055	0.058	0.061	0.061
$\xi_0 \times 10^{10}$ (m)	2.6	1.9	1.9	1.3	1.7	1.6	1.5	1.5	2.2	1.8	1.3	1.3
$H_0 \times 10^{-3}$ (m)	0.287	0.525	0.536	0.575	0.617	0.927	1.10	1.61	1.64	2.40	6.20	6.96
$\lambda_0 \times 10^2$	1.12	1.23	1.14	1.05	1.10	1.02	0.99	1.00	1.11	0.98	1.00	0.99
$\tau_0 \times 10^6$	0.946	0.305	0.356	0.280	0.318	0.256	0.209	0.167	0.208	0.172	0.086	0.082
$\zeta_0 \times 10^{10}$ (m)	1.37	2.05	1.86	1.44	1.80	1.92	2.12	2.41	3.01	2.87	3.08	3.20
$s_0 \times 10^{10}$ ($N \cdot m^{-1}$)	0.08	3.7	4.3	1.0	3.2	1.9	1.3	2.7	2.3	1.7	3.2	3.2
$\lvert d\rho^*/dz \rvert_c$ ($\% \cdot \mu m^{-1}$)	0.78	0.58	0.59	0.70	0.59	0.51	0.45	0.40	0.35	0.33	0.31	0.30
$\xi_{\parallel,c}$ (μm)	0.7	1.1	1.0	0.7	0.9	1.0	1.1	1.2	1.6	1.5	1.6	1.6
$\xi_{\perp,c}$ (μm)	1.2	1.8	1.7	1.3	1.6	1.7	1.9	2.1	2.7	2.6	2.7	2.8
L_{max} (μm)	2.9	4.4	4.0	3.1	3.9	4.1	4.5	5.2	6.4	6.1	6.6	6.8
$\Delta T_+ - \Delta T_-$ (mK)	0.05	1.5	1.6	0.2	1.0	0.6	0.4	0.8	1.3	0.7	0.8	0.8

[a] $\beta = 0.325$, $\gamma = 1.240$, $\delta = (\beta + \gamma)/\beta$, $\alpha = 2 - 2\beta - \gamma$, and $\nu = (2\beta + \gamma)/3$.

Ising-like systems [8]. The amplitudes B, Γ, D, and ξ_0 depend on the system but are interrelated by the universal amplitude combinations

$$R_D = D\Gamma B^{\delta-1} = \frac{D\Gamma}{x_0^{\gamma}} \simeq 1.74; \qquad R_\xi = \xi_0 \left(\frac{B^2 P_c}{k_B T_c}\right)^{1/3} \simeq 0.69 \tag{11}$$

where k_B is Boltzmann's constant. Values of the critical parameters P_c, ρ_c, and T_c, the critical power-law amplitudes x_0, D, Γ, and ξ_0, and the gravity scale factor H_0 are presented in Table I for a number of fluids.

Substitution of the scaling laws into the differential equation yields

$$A_0 \frac{d^2 |\Delta\rho^*|}{dz^2} = \frac{1}{D^2 H_0^2} \left[|\Delta\rho^*|^{\delta} h(u) - \frac{g^* z}{D H_0} \right] G(u) |\Delta\rho^*|^{\eta\nu/\beta} \tag{12}$$

with $\eta\nu = 2\nu - \gamma$ and

$$A_0 = \frac{\xi_0^2 R^2(0)}{D^2 H_0^2 (D\Gamma)^{2\nu/\gamma} \delta^{\eta\nu/\gamma}} \tag{13}$$

The scaling function $G(u)$ is related to the scaling functions $X(u)$ and $R(u)$ by

$$G(u) = \frac{R^2(0)}{R^2(u)} \left[\frac{X(u)}{X(0)}\right]^{\eta\nu/\gamma} \tag{14}$$

3. SCALING LAWS AND UNIVERSALITY IN THE PRESENCE OF GRAVITY

The scaling laws can be generalized to include the effect of gravity. For this purpose we rescale the variables such that [5]

$$\Delta\rho^* = \lambda_0 g^{*\beta\phi} \overline{\Delta\rho}, \qquad \Delta T^* = \tau_0 g^{*\phi} \overline{\Delta T}, \qquad z = \zeta_0 g^{*-\nu\phi} \bar{z} \tag{15}$$

with

$$\phi = \frac{1}{\beta\delta + \nu} \tag{16}$$

The scale factors λ_0, τ_0, and ζ_0 are defined by

$$\lambda_0 = A_0^{\beta\phi/2}, \qquad \tau_0 = x_0 A_0^{\phi/2}, \qquad \zeta_0 = D H_0 A_0^{\beta\delta\phi/2} \tag{17}$$

In terms of these rescaled variables the differential equation (12) assumes the form

$$\frac{d^2 |\overline{\Delta\rho}|}{d\bar{z}^2} = [|\overline{\Delta\rho}|^{\delta} h(u) - \bar{z}] \, G(u) |\overline{\Delta\rho}|^{\eta\nu/\beta} \tag{18}$$

with $u = \overline{\Delta T}/|\overline{\Delta\rho}|^{1/\beta}$. Since the critical exponents and the scaling functions are universal, it follows from (18) that the scaled density $\overline{\Delta\rho}$ will be a universal function of the scaled height $\bar{z}$ and the scaled temperature $\overline{\Delta T}$, We thus conclude that in the presence of gravity the density $\Delta\rho^*$ satisfies a scaling law of the form

$$\Delta\rho^*(z, \Delta T^*) = \lambda_0 \, g^{*\beta\phi} \, \overline{\Delta\rho} \left(\frac{z}{\zeta_0 \, g^{*-\nu\phi}}, \frac{\Delta T^*}{\tau_0 \, g^{*\phi}} \right) \tag{19}$$

where $\overline{\Delta\rho}$ is a universal function of its variables. The corresponding scaling law for the surface tension σ becomes [9]

$$\sigma(\Delta T^*) = s_0 \, g^{*2\nu\phi} \, \bar{\sigma} \left(\frac{\Delta T^*}{\tau_0 \, g^{*\phi}} \right) \tag{20}$$

with

$$s_0 = P_c D \lambda_0^{\delta+1} \zeta_0 = P_c D^2 H_0 A_0^{\beta(2\delta-1)\phi|2} \tag{21}$$

It is interesting to note that the validity of these scaling laws is not subject to the limitations of the squared-gradient theory. The scaling laws (8) and (10) imply that $\Delta\mu^*(\rho, T)$ and $\xi(\rho, T)$ are generalized homogeneous functions of the form

$$\Delta\mu^*(b^{-\beta/\nu} \Delta\rho^*, b^{-1/\nu} \Delta T^*) = b^{-\beta\delta/\nu} \Delta\mu^*(\Delta\rho^*, \Delta T^*) \tag{22}$$

$$\xi(b^{-\beta/\nu} \Delta\rho^*, b^{-1/\nu} \Delta T^*) = b\xi(\Delta\rho^*, \Delta T^*) \tag{23}$$

for any values of the parameter b. In terms of the concepts of the renormalization-group theory, this result is to be interpreted as follows [3]. If we scale all distances, and hence the correlation length ξ, with a factor b, then $\Delta\rho^*$ scales with a factor $b^{-\beta/\nu}$, ΔT^* with a factor $b^{-1/\nu}$, and $\Delta\mu^*$ with a factor $b^{-\beta\delta/\nu}$. Since the gravitational potential gz contributes to the effective chemical potential, we expect gz also to scale with a factor $b^{-\beta\delta/\nu}$ as does $\Delta\mu^*$. Since z will scale with a factor b, g will scale with a factor $b^{-\beta\delta/\nu}/b = b^{-1/\nu\phi}$. We thus expect that

$$\Delta\rho^*(b^{-1/\nu\phi} g, bz, b^{-1/\nu} \Delta T^*) = b^{-\beta/\nu} \Delta\rho^*(g, z, \Delta T^*) \tag{24}$$

Substitution of $b = g^{\nu\phi}$ in (24) reproduces the scaling law (19).

4. DENSITY PROFILES IN THE ONE-PHASE REGION ABOVE T_c

In the one-phase region, that is for $u > -1$, the scaling functions $h(u)$ and $R(u)$ are known with reasonable accuracy and can be approximated by [5]

$$h(u) = (1+u)\left[\frac{1+E(1+u)^{2\beta}}{1+E}\right]^{(\gamma-1)/2\beta} \tag{25}$$

$$R(u) = \frac{8+u}{7+u} \tag{26}$$

with $\beta = 0.325$, $\gamma = 1.240$, and $E = 0.287$.

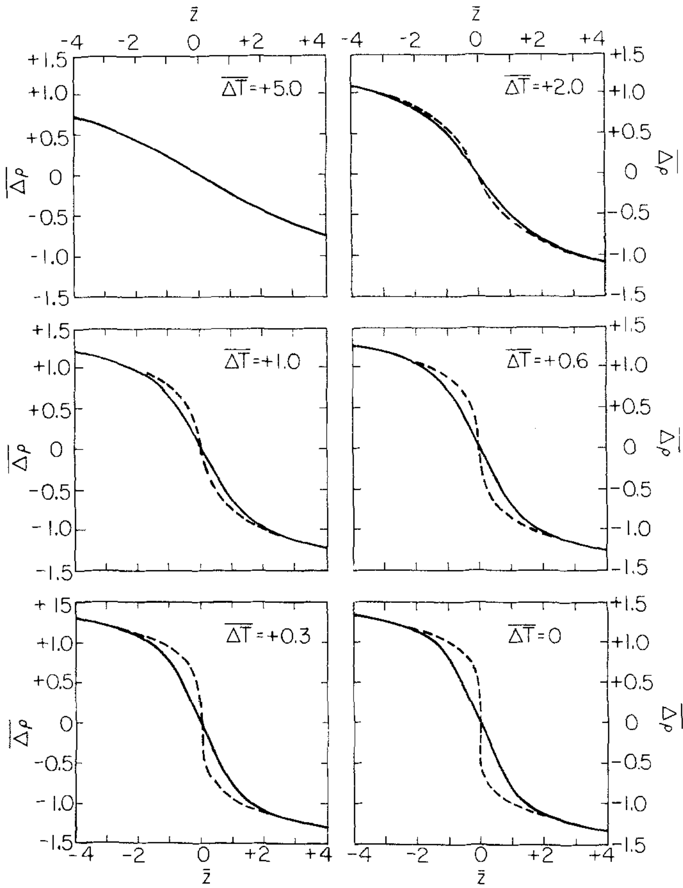

Fig. 1. Density $\overline{\Delta\rho}$ as a function of the height $\bar{z}$ at various temperatures above T_c. The solid curves represent the actual density profiles in the presence of gravity. The dashed curves are those obtained if one neglects the effects of the $d^2\overline{\Delta\rho}/d\bar{z}^2$ term on the profiles.

Using these approximants for the scaling functions we have solved the differential equation (18). Density profiles thus obtained are shown in Fig. 1 for a few selected temperatures [5]. In Fig. 1 we also show the profiles obtained if one neglects the $d\rho^2/dz^2$ term, which accounts for the interaction between the layers; in that case the profile would be determined by $|\overline{\Delta\rho}|^\delta h(u) = \bar{z}$, which implies that the density gradient at the layer $z = 0$ corresponding to $\rho = \rho_c$ would diverge as

$$\left|\frac{d\overline{\Delta\rho}}{d\bar{z}}\right|_{\bar{z}=0} = \frac{D\Gamma}{x_0^\gamma} |\overline{\Delta T}|^{-\gamma} \simeq 1.74 |\overline{\Delta T}|^{-\gamma} \tag{27}$$

The actual density gradient does not diverge but reaches, at the critical point, the value [5]

$$\lim_{\overline{\Delta T}\to 0} \left|\frac{d\overline{\Delta\rho}}{d\bar{z}}\right|_{\bar{z}=0} = \left|\frac{d\overline{\Delta\rho}}{d\bar{z}}\right|_{c} = 0.96 \tag{28}$$

The corresponding values for the density gradient $|d\Delta\rho^*/dz|_c$ in fluids in the earth's gravitational field are included in Table I. This gradient varies from 0.8 %/μm in ^{3}He to 0.3 %/μm in steam.

It turns out that the intrinsic gravity effects, i.e., the differences between the solution of the differential equation (18) and the approximate solution $\bar{z} = |\overline{\Delta\rho}|^\delta h(u)$ become significant at temperatures $\overline{\Delta T}$ for which [5]

$$\overline{\Delta T} \leqslant \overline{\Delta T}_+ = 6 \tag{29}$$

5. DENSITY PROFILES IN THE TWO-PHASE REGION BELOW T_c

In order to extend the theory to the two-phase region below T_c we need expressions for the scaling functions for densities between those of the coexisting vapor and liquid phases, i.e., for $u < -1$. Here we follow the procedure of Fisk and Widom [4,6] by using a classical interpolation function but with nonclassical values for the critical exponents. The differential equation (18) then reduces for $u < -1$ to [9]

$$\frac{d^2|\overline{\Delta\rho}|}{dz^2} = \{a[|\overline{\Delta\rho}|^\delta - |\overline{\Delta T}|^\gamma |\overline{\Delta\rho}|] - \bar{z}\}\, G(-1) |\overline{\Delta T}|^{\eta\nu} \tag{30}$$

The constant a is determined by the condition that the compressibility be continuous at the phase boundary, which implies $a = X(-1)/(\delta - 1) = \gamma^{-1}(1+E)^{(1-\gamma)/2\beta}$.

To obtain the density profiles below T_c we thus use (30) for $u < -1$, supplemented with (18) for the vapor and liquid regions, i.e., for $u > -1$. Density profiles thus obtained are shown in Fig. 2 for a few selected temperatures [9]. In Fig. 2 we also show the profiles obtained from the theory of Fisk and Widom in which gravity effects are neglected [4, 6]. The theory of Fisk and Widom without gravity is obtained if the $\bar{z}$ term on the

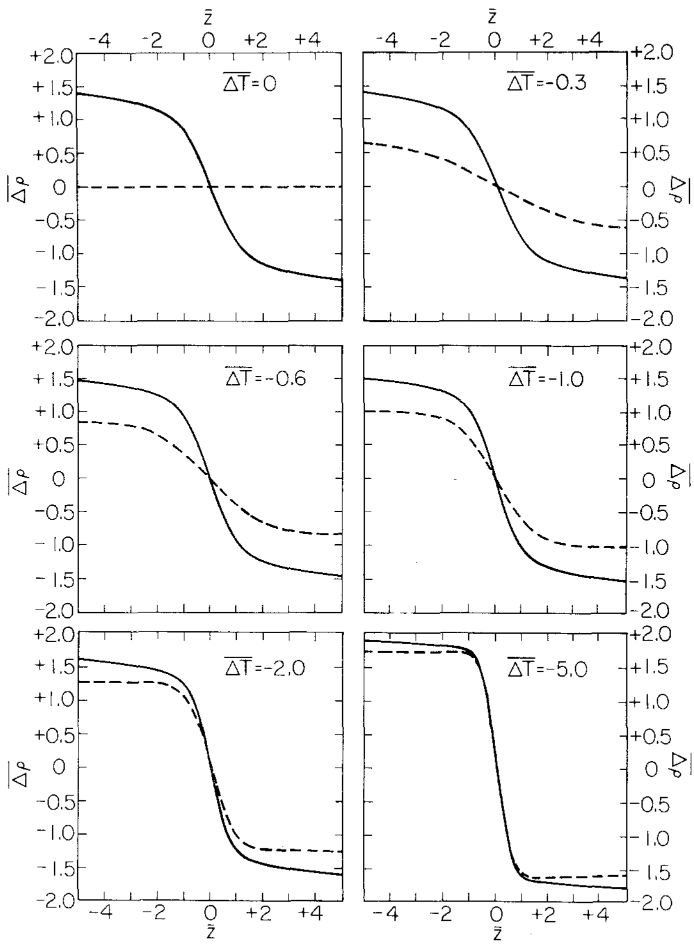

Fig. 2. Density $\overline{\Delta\rho}$ as a function of the height $\bar{z}$ at various temperatures below T_c. The solid curves represent the actual density profiles in the presence of gravity. The dashed curves represent the density profiles calculated from the theory of Fisk and Widom without gravity effects.

right-hand side of (30) is deleted; it predicts that the density gradient at the layer $z=0$ coresponding to $\rho=\rho_c$ would go to zero as [9]

$$\left|\frac{d\overline{\Delta\rho}}{d\bar{z}}\right|_{\bar{z}=0}=\left[\frac{aG(-1)(\delta-1)}{\delta+1}\right]^{1/2}|\overline{\Delta T}|^{\beta+\nu}\simeq 0.677\,|\overline{\Delta T}|^{\beta+\nu} \tag{31}$$

In reality this density gradient approaches at the critical point the same value $|d\overline{\Delta\rho}/d\bar{z}|_c=0.96$ as when the critical point is approached from above.

On comparing Figs. 1 and 2 we conclude that the density profiles in the one-phase region above T_c are smoothly connected with the density profiles in the two-phase region below T_c. This phenomenon is further illustrated in Fig. 3, where we have plotted the density gradient $|d\overline{\Delta\rho}/d\bar{z}|_{\bar{z}=0}$ as a function of the temperature. This density gradient crosses over from the power law (27) well above T_c to the power law (31) well below T_c.

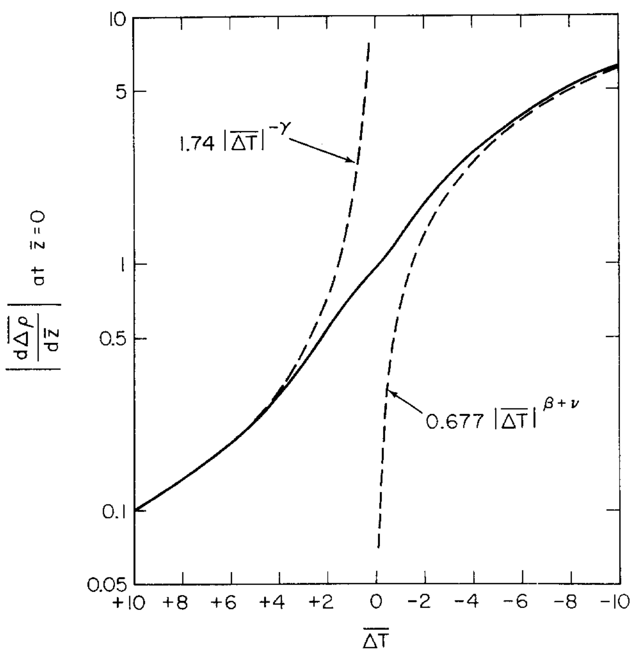

Fig. 3. Density gradient $|\overline{\Delta\rho}/d\bar{z}|$ at $\bar{z}=0$ as a function of $\overline{\Delta T}$. The solid curve represents the actual behavior of the density gradient in the presence of gravity. The dashed curve for $\overline{\Delta T}>0$ indicates the power law (27) obtained if one neglects the effect of the $d^2\overline{\Delta\rho}/d\bar{z}^2$ term on the profiles. The dashed curve for $\overline{\Delta T}<0$ indicates the power law (31) obtained from the theory of Fisk and Widom without gravity effects.

We define the thickness $L = \zeta_0 g^{*-\nu\phi} \bar{L}$ of the interface as the distance over which the density changes from that of the liquid at the phase boundary to that of the vapor at the phase boundary. The scaled interface thickness $\bar{L}$ is plotted in Fig. 4 as a function of the temperature. In the theory of Fisk and Widom without gravity, the interface thickness is predicted to diverge as $|\overline{\Delta T}|^{-\nu}$. We find that for $|\overline{\Delta T}| \gg 1$ the interface thickness satisfies an equation of the form [9]

$$\bar{L} = -\frac{2}{C|\overline{\Delta T}|^{\nu}} \ln\left[\frac{G(-1)|\overline{\Delta T}|^{-\beta\delta}\bar{L}}{2C^2 V_0}\right] \tag{32}$$

with $C^2 = aG(-1)(\delta - 1)$ and $V_0 \simeq 2.9$. For $|\overline{\Delta T}| \ll 1$, the interface thickness goes to zero as [9]

$$\bar{L} = \frac{2}{|d\overline{\Delta\rho}/d\bar{z}|_c} |\overline{\Delta T}|^{\beta} \simeq 2.08 |\overline{\Delta T}|^{\beta} \tag{33}$$

Thus the interface thickness first increases when the critical temperature is approached from below, reaches a maximum value

$$\bar{L}_{\max} = 2.14 \tag{34}$$

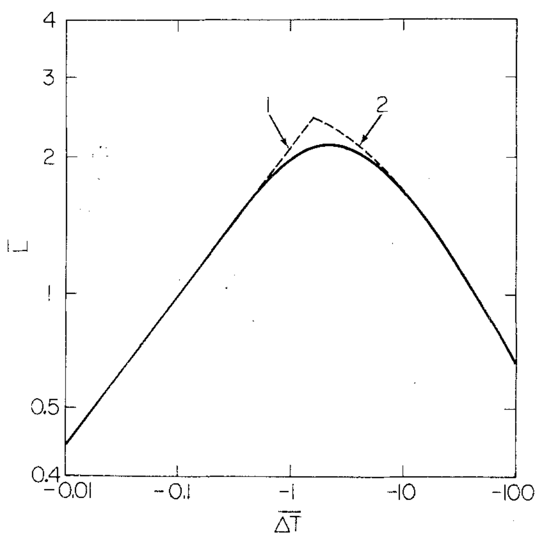

Fig. 4. Interface thickness $\bar{L}$ as a function of $\overline{\Delta T}$. The solid curve represents the actual interfacial width in the presence of gravity. The dashed curve labeled 1 represents the asymptotic power law (33) for small $|\overline{\Delta T}|$; the dashed curve labeled 2 represents the asymptotic behavior (32) for large $|\overline{\Delta T}|$.

at a temperature $\overline{\Delta T} = -2.2$, and then goes to zero upon closer approach to T_c.

Values for the maximum vapor–liquid interface thickness to be expected in the earth's gravitational field are included in Table I. This maximum interface thickness is of the order of a few micrometers.

The theory presented here is incomplete in that it does not include the effects of capillary waves on the interface thickness [4, 10, 11]. However, the capillary wave effects are small in the temperature range we have considered here [9].

6. SURFACE TENSION

The theory of Fisk and Widom without gravity predicts that the surface tension will asymptotically vanish as

$$\bar{\sigma} = \bar{\sigma}_0 |\overline{\Delta T}|^{2\nu} \simeq 0.99 |\overline{\Delta T}|^{2\nu} \tag{35}$$

where $\bar{\sigma}$ is the scaled surface tension defined by (20). The actual behavior of this scaled surface tension as a function of temperature is shown in Fig. 5. We find that in the presence of gravity the surface tension vanishes as [9]

$$\bar{\sigma} = \frac{2 |d\overline{\Delta\rho}/d\bar{z}|_c}{G(-1)} |\overline{\Delta T}|^{\beta - \eta\nu} \simeq 2 |\overline{\Delta T}|^{\beta - \eta\nu} \tag{36}$$

We mentioned earlier that the squared-gradient theory cannot deal correctly with the deviations of the correlation function from the Ornstein-Zernike theory which are of the order of the exponent η. Strictly speaking, therefore, within the limitations of the present theory we cannot discriminate between an asymptotic power law for the surface tension proportional to $|\overline{\Delta T}|^{\beta-\eta\nu}$ or proportional to $|\Delta\bar{T}|^{\beta}$.

We find that the actual surface tension will differ from the power law (35) expected without gravity at temperatures for which

$$|\overline{\Delta T}| \leqslant |\overline{\Delta T}_-| = 9 \tag{37}$$

On comparing with (29) we conclude that intrinsic gravity effects are present in a temperature range

$$\overline{\Delta T}_+ - \overline{\Delta T}_{-1} = 15 \tag{38}$$

The corresponding temperature range for intrinsic gravity effects in fluids in the earth's gravitational field is included in Table I. For most fluids this temperature range is of the order of a millidegree.

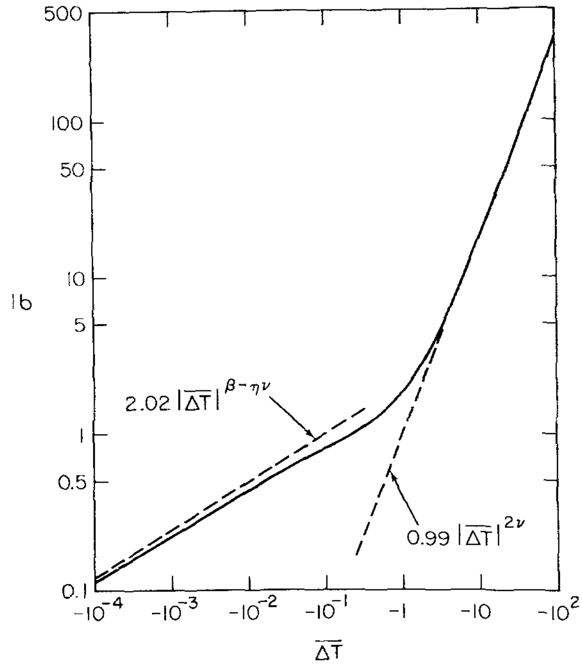

Fig. 5. Surface tension $\bar{\sigma}$ as a function of $\overline{\Delta T}$. The solid curve represents the actual interfacial tension in the presence of gravity. The dashed curves represent the asymptotic equations (36) and (35) for small and large values of $|\overline{\Delta T}|$.

7. CORRELATION LENGTH

The squared-gradient theory can be extended to the correlation function. In a homogeneous system the correlation length ξ diverges at the critical point. In the presence of gravity the correlation function becomes anisotropic and we distinguish between a correlation length $\xi_{\|}(z, \Delta T^*)$ parallel to the gravitational field and a correlation length $\xi_{\perp}(z, \Delta T^*)$ perpendicular to the gravitational field. These correlation lengths satisfy the scaling laws

$$\xi_{\|}(z, \Delta T^*) = \zeta_0 g^{*-\nu\phi} \bar{\xi}_{\|}\left(\frac{z}{\zeta_0 g^{*-\nu\phi}}, \frac{\Delta T^*}{\tau_0 g^{*\phi}}\right) \tag{39}$$

$$\xi_{\perp}(z, \Delta T^*) = \zeta_0 g^{*-\nu\phi} \bar{\xi}_{\perp}\left(\frac{z}{\zeta_0 g^{*-\nu\phi}}, \frac{\Delta T^*}{\tau_0 g^{*\phi}}\right) \tag{40}$$

In a previous paper we have evaluated the two correlation lengths $\bar{\xi}_{\parallel}$ and $\bar{\xi}_{\perp}$ as a function of $\bar{z}$ and $\overline{\Delta T}$ in the one-phase region above the critical temperature [12]. An investigation of these correlation lengths in the vapor–liquid interface below the critical temperature will be published elsewhere [13].

Since the results have been discussed in considerable detail in a previous publication [14], we consider here only the behavior of these correlation lengths at the critical temperature. The scaled correlation lengths $\bar{\xi}_{\parallel}$ and $\bar{\xi}_{\perp}$ are plotted as a function of the scaled height $\bar{z}$ in Fig. 6. In the same figure we also show the correlation length $\bar{\xi}(\rho(z), T_c)$ calculated in the locally homogeneous approximation. In the locally homogeneous approximation $\bar{\xi}(\rho(z), T_c)$ diverges at $\rho(0) = \rho_c$. The actual correlation lengths $\bar{\xi}_{\parallel}$ and $\bar{\xi}_{\perp}$ remain finite at $\rho = \rho_c$, where they reach the values [12]

$$\bar{\xi}_{\parallel,c} = 0.515, \qquad \bar{\xi}_{\perp,c} = 0.889 \tag{41}$$

The corresponding values of the correlation lengths $\xi_{\parallel,c}$ and $\xi_{\perp,c}$ for fluids in the earth's gravitational field are included in Table I. The maximum values of the correlation length in fluids in the earth's gravitational field are of the order of 2 μm.

From Fig. 6 we note that the correlation length $\bar{\xi}_{\perp}$ perpendicular to the gravitational field reaches its maximum value at the critical layer $\bar{z} = 0$ where $\rho = \rho_c$, but the correlation length $\bar{\xi}_{\parallel}$ reaches its maximum value $1.4\,\bar{\xi}_{\parallel,c}$ at a layer slightly above and below the critical layer. The latter

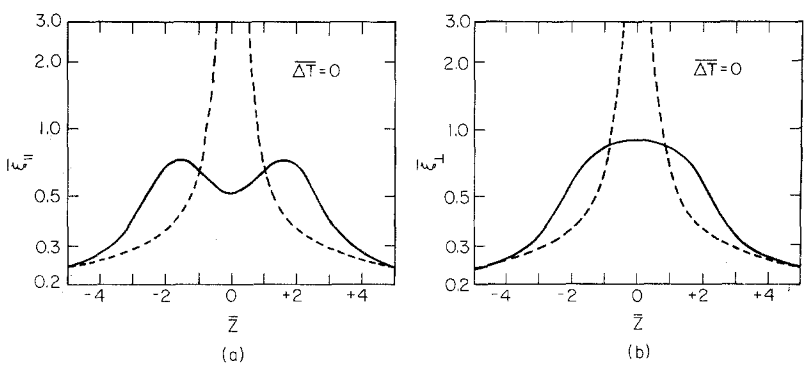

Fig. 6. The correlation lengths $\bar{\xi}_{\parallel}$ and $\bar{\xi}_{\perp}$ as a function of the height $\bar{z}$ at the critical temperature. The solid curves represent the actual correlation lengths parallel to the gravitational field ($\bar{\xi}_{\parallel}$) and perpendicular to the gravitational field ($\bar{\xi}_{\perp}$). The dashed curves represent the correlation length $\bar{\xi}(\rho(z), T_c)$ calculated in the locally homogeneous approximation.

effect is a consequence of the asymmetry induced in the correlation function in the direction parallel to the gravitational field. For a further discussion the reader is referred to previous publications [12, 14].

ACKNOWLEDGMENTS

We acknowledge stimulating discussions with M. Robert and B. Widom. The research was supported by National Science Foundation—Low Temperature Physics—Grant DMR 82-05356 and by NATO Research Grant 008.81.

REFERENCES

1. J. M. H. Levelt Sengers, in *Experimental Thermodynamics II*, B. Le Neindre and B. Vodar, eds. (Butterworths, London, 1975), p. 657.
2. M. R. Moldover, J. V. Sengers, R. W. Gammon, and R. J. Hocken, *Rev. Mod. Phys.* **51**:79 (1979).
3. C. Domb and M. S. Green, eds., *Phase Transitions and Critical Phenomena* (Academic Press, New York, 1976).
4. J. S. Rowlinson and B. Widom, *Molecular Theory of Capillarity* (Clarendon Press, Oxford, 1982).
5. J. V. Sengers and J. M. J. van Leeuwen, *Physica* **116A**:345 (1982).
6. S. Fisk and B. Widom, *J. Chem. Phys.* **50**:3219 (1969).
7. J. V. Sengers and J. M. H. Levelt Sengers, in *Progress in Liquid Physics*, C. A. Croxton, ed. (Wiley, New York, 1978), p. 103.
8. M. Levy, J. C. Le Guillou, and J. Zinn-Justin, eds., *Phase Transitions: Cargèse 1980* (Plenum Press, New York, 1982).
9. J. M. J. van Leeuwen and J. V. Sengers, *Physica* **132A**:207 (1985).
10. D. Jasnow, *Rep. Progr. Phys.* **47**:1059 (1984).
11. D. A. Huse, W. van Saarloos, and J. D. Weeks, *Phys. Rev. B* **32**:233 (1985).
12. J. M. J. van Leeuwen and J. V. Sengers, *Physica* **128A**:99 (1984).
13. J. H. Sikkenk, J. M. J. van Leeuwen, and J. V. Sengers, *Physica A* (in press).
14. J. V. Sengers and J. M. J. van Leeuwen, *J. Phys. Chem.* **88**:6479 (1984).