Hydrodynamics of fluids near a critical point

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Because many properties of a fluid are highly anomalous near a critical point, experimental situations that normally are very simple to describe become much more complicated. Thus the specific heat of a sample is different from bulk values because of large, gravity-induced density gradients. The problems of relaxation to equilibrium, free convection, Brownian motion of a particle, and the viscous damping of an oscillating cylinder or a rotating disk are all complicated by the large compressibility, and, in general, the need to solve the hydrodynamic equations in a nonlinear regime.

CONTENTS

I. INTRODUCTION

A. Critical phenomena

The liquid–vapor critical point of a one-component fluid is fixed by the conditions (Landau and Lifshitz, 1958)

$$\left(\frac{\partial p}{\partial \rho}\right)_T=\left(\frac{\partial^2 p}{\partial \rho^2}\right)_T=0\ , \tag{1.1}$$

where p is the pressure, ρ is the density, and T is the temperature.

Similarly, the critical points of binary mixtures are characterized by the vanishing of the first two derivatives of the chemical potential μ with respect to the concentration c

$$\left(\frac{\partial \mu}{\partial c}\right)_{p,T}=\left(\frac{\partial^2 \mu}{\partial c^2}\right)_{p,T}=0\ . \tag{1.2}$$

Here $\mu=\mu_1/m_1-\mu_2/m_2$, where μ_1,μ_2 and m_1,m_2 are the chemical potentials and masses of the components, respectively.

The infinite increase of the compressibility $(1/\rho)(\partial\rho/\partial p)_T$ [or the susceptibility $(\partial c/\partial\mu)_{p,T}$] as the critical point is approached leads to a number of peculiarities in the behavior of a substance near its critical point. The specific heat at constant pressure c_p and heat expansion coefficient

$$\beta=-\frac{1}{\rho}\left(\frac{\partial\rho}{\partial T}\right)_p$$

also increase towards the critical point of a fluid, as follows from Eq. (1.1) and the appropriate thermodynamic relations.

A sharp increase in the mean square of the fluctuations of the density (or concentration) and of the integral of the correlation function of these fluctuations $g_{\rho\rho}$ already follows from the well-known thermodynamic relations:

$$\begin{aligned}&\overline{[\rho(r)-\bar{\rho}]^2}\sim\left(\frac{\partial\rho}{\partial p}\right)_T\to\infty\\&\int g_{\rho\rho}d^3r\sim\left(\frac{\partial\rho}{\partial p}\right)_T\to\infty\ .\end{aligned} \tag{1.3}$$

The large increase of the correlations between the positions of different particles is given by the second expression in (1.3), and this is closely connected with the first expression there. In other words, widely separated particles have to be strongly correlated to cause great changes of the density.

The correlation radius ξ which characterizes the distances over which correlation is significant increases sharply close to the critical temperature T_c, i.e.,

$$\xi\,|_{T\to T_c}\to\infty\ . \tag{1.4}$$

According to estimates from scattering experiments it reaches a value of 10^{-4}–10^{-5} cm near the critical point.

Thus the specific nature of the critical region consists in the appearance of a new characteristic distance ξ, satisfying

$$a\ll\xi\ll L\ , \tag{1.5}$$

where a is the average distance between particles, and L is the characteristic macroscopic length.

As an illustration of the crucial importance of new characteristic length ξ let us find the singular part of the transport coefficients near the critical point for a

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model of the fluid near the critical point consisting of spheres with a characteristic radius ξ. Particles inside such spheres are strongly correlated and we can assume that under the influence of external forces they move together with a mean velocity v and with a mean free path ξ. We find the following results:

1. Diffusion coefficient (Arcovito *et al.*, 1969). When an external force F is applied the spheres move according to Stoke's law: $F \sim \eta\xi v$ where η is the viscosity, i.e., their mobility is $b \equiv (v/F) \sim 1/\eta\xi$. Using the Einstein relation for the diffusion coefficient D, $D = k_B T b$ (where k_B is the Boltzman constant), we have $D \sim 1/\eta\xi$ or $D\eta \sim 1/\xi$, a result confirmed by accurate theory and by experiment.

2. Heat conductivity. Using the usual arguments of the molecular-kinetic theory we can find the heat flux q passing through unit area per unit time: $q \sim vn(\epsilon_1 - \epsilon_2)$. Here n is the total number of spheres and $\epsilon_1 - \epsilon_2$ is the difference in their energies on two sides of a selected area, arising from the temperature difference $T_1 - T_2 \sim \xi\nabla T$: $\epsilon_1 - \epsilon_2 \sim VC_p\xi\nabla T$, where V is the total volume of the spheres, so that $nV \sim 1$. Thus $q \sim vC_p\xi\nabla T$. To find v we can use the estimate for the diffusion coefficient given above: $v \sim \xi/t_c \sim \xi D/\xi^2 \sim 1/\eta\xi^2$. Finally we have for the heat conductivity $\lambda \sim q/\nabla T \sim vC_p\xi \sim C_p(\eta\xi)^{-1}$. This result is supported by more rigorous theory and also by experiment.

Apart from the above-mentioned "strong" singularities of thermodynamic values at the critical point, "weak" singularities have also been found recently. An example is the singularity of the specific heat at constant volume C_V, which causes the adiabatic velocity of sound to approach zero towards the critical point (Bagatskii *et al.*, 1962).

At the same time relaxation processes slow down as a result of the increase of the correlation radius and the decrease of the sound velocities. There are corresponding anomalies in the behavior of binary mixtures near the critical point, as a consequence of (1.2).

We see therefore that fluids near their critical points are fascinating physical systems: they are highly compressible and slowly fluctuating inhomogeneous media with long-range correlations.

Considerable advances have been made in the theoretical explanation of the asymptotic dependences of thermodynamic values on the proximity of the critical point and in the establishment of equations of state. All these problems are beyond the scope of our article and we refer the reader to comprehensive reviews (Wilson and Kogut, 1974). Significant success has also been achieved in the study of the behavior of kinetic coefficients near the critical points of one-component fluids and binary mixtures (Swinney and Henry, 1973; Halperin *et al.*, 1974; Siggia *et al.*, 1976).

In addition to the microscopic approach there is an alternative way of describing critical phenomena, namely the hydrodynamic description, which is made possible by the existence of the characteristic macroscopic length (1.4). This review discusses some problems of critical behavior within the framework of hydrodynamic theory. We should point out, however, that we do not attempt a comprehensive experimental or even theoretical survey of hydrodynamics of critical phenomena.

It is interesting that the first systematic theory of order–disorder phenomena (including the critical points), Landau's mean field approximation, is a hydrodynamic theory (Landau, 1937; Landau and Lifshitz, 1958).

According to this theory the free energy per unit volume F can be expanded into a power series in a so-called order parameter $\eta(r)$ responsible for the phase transition:

$$F(r) = F_0 + A[\eta(r)]^2 + B[\eta(r)]^4 + \cdots . \tag{1.6}$$

The equilibrium value of η is determined from the condition $\partial F/\partial\eta = 0$. The macroscopic approach in (1.6) means that the discrete atomic structure is neglected and any infinitesimal element of volume is always supposed to be large enough to contain a large number of atoms. Accordingly the "point" r in (1.6) signifies the existence of some hydrodynamic scale r_{hyd} large compared with the average distance between atoms "a" but small compared with the characteristic distance L of the problem under consideration:

$$a \ll r_{\text{hyd}} \ll L . \tag{1.7}$$

Of course, in such theories it is assumed that all physical results, in particular the thermodynamic parameters A, B, and all functions of them, do not depend on the choice of r_{hyd}.

In the framework of the renormalization group theory (Wilson and Kogut, 1974) not only the average values of $\eta(r)$ but also fluctuations with wavelengths $\lambda < r_{\text{hyd}}$ are taken into account. One of the results of this theory is the dependence of A and B on r_{hyd} in contradiction with the essence of Landau's theory. Actually it has been found that the mean field theory is of zero order in the expansion parameter $\epsilon = d - 4$, where d is the dimensionality of space.

Qualitatively all restrictions of Landau's theory were clear from the beginning. Apart from the often noticed impropriety of using a power series in (1.6) near the singularity points, the original hydrodynamics approach also breaks down near the critical point. Far from T_c all microscopic distances (average distance between particles, range of force, and correlation radius) are of the same order of magnitude. But near T_c, according to (1.4) $\xi \to \infty$. Then the application of the hydrodynamic theory is problematic when $\xi \gtrsim r_{\text{hyd}}$, and wrong when $\xi \gtrsim L$.

Thus a demand arose for a renewed consideration of the typical hydrodynamic problems for fluids near their critical points. Only those problems will be prominent in our considerations which have a close connection with existing experiments or which may lead to new experiments for studying the critical behavior of fluids.

Let us discuss first whether the usual hydrodynamic theory can be applied to the critical fluid.

B. Hydrodynamic theory

The hydrodynamic approach is based on the following four components:

1. Macroscopic approach.
2. Conservation laws for five thermodynamic variables characterizing the local-equilibrium state of the pure fluid (Landau and Lifshitz, 1963)

$$\frac{d\rho(r,t)}{dt}=0;\quad \frac{dv_i(r,t)}{dt}=-\frac{\partial P_{ik}}{\partial x_k};\quad \rho\frac{de(r,t)}{dt}=-\nabla q-P_{ik}D_{ik}$$

where

$$D_{ik}=\frac{1}{2}\left(\frac{\partial v_i}{\partial x_k}+\frac{\partial v_k}{\partial x_i}\right),$$

e is the energy density, P_{ik} the flux of momentum, and q the flux of heat.

3. Equation of state, i.e., the connection between hydrodynamic local variables $\rho(r,t)$, $v(r,t)$, and $\epsilon(r,t)$.

4. Connection between P_{ik} and q, and the driving forces which are functions of ρ, v, ϵ.

Let us discuss these components in a little more detail.

In the case of a dilute system (gas) we have, in increasing magnitudes, the three time scales shown in Fig. 1. Each region has its corresponding description. In solids the situation is reversed: the "mean free time" τ_m is much less than the "collision time" τ_{coll}. In the intermediate liquid region they are of the same order of magnitude. At the same time, the ratio of the characteristic potential and kinetic energies is much smaller or larger than unity for the gas and solid, respectively, but is of the order of unity for liquids. The absence of a small parameter is the well-known difficulty in the development of the theory of liquids.

As a basis for description of small departures from equilibrium, the difference between the slow macroscopic characteristic times and the fast decay time of the correlation functions of dynamic variables can be used. Up to 1967 it was thought that such an approximation was good enough. Recent results derived first in computer simulation for hard spheres and disks (Alder and Wainwright, 1967) and then by different methods (Ernst *et al.*, 1971; Kawasaki, 1970b, 1971; Dorfman and Cohen, 1972; Keyes and Oppenheim, 1973a) have shown that the autocorrelation functions for, say, velocity have a power rather than an exponential decay:

$$\overline{v(t)v(0)}\sim 1/t^{d/2}, \tag{1.9}$$

where d is the dimensionality of space.[1] These results narrow the difference between macroscopic and microscopic characteristic times and prevent the application of the hydrodynamic equations to phenomena that vary on a long enough time scale. The difficulties increase near the critical points where the above-mentioned growth of characteristic distances is accompanied by a corresponding decrease of characteristic times.

The conservation laws are exact, but additional complications appear when we pass to the problem of an equation of state for the fluctuations described, according to Onsager's assumption, by the hydrodynamic equations.

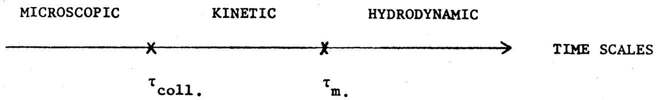

FIG. 1. Time scales for different processes in gases; τ_{coll} is the characteristic time of collisions between particles, τ_m is a mean free time. Each region has its corresponding description (microscopic, kinetic, and hydrodynamic).

Generally speaking the fluctuations are independent or are only correlated, i.e., there is not a unique relation between them. However, we indicated above that two scales of distances exist—the macroscopic correlation radius of the order parameter (1.4) and the microscopic characteristic distance for all other variables. Similarly it is natural to assume that two characteristic time scales exist: a time for dissipation of some characteristic parameter which tends to infinity upon approaching the critical point, and a time for the establishment of equilibrium in the remaining variables, whose fluctuations do not possess anomalies at the critical point. Such an "adiabatic approximation" means that for a given nonequilibrium (fluctuation) distribution of the order parameter the remaining thermodynamical variables assume definite values. This assumption is analogous to the assumption of incomplete equilibrium used in the theory of so-called thermodynamic fluctuations of the quantity x (Landau and Lifshitz, 1959). The relaxation time for establishing incomplete equilibrium corresponding to a specified value of x is assumed to be much less than the relaxation time for the quantity x itself. One is able to formulate an equation of state in the sense of a nonlocal and nonsynchronous relation between the change of the pressure (chemical potential) and the distribution of the densities (concentration) (Gitterman and Kontorovich, 1964; Gitterman and Gorodetskii, 1969):

$$p(r,t)-p_0=\int Q(r-r',t-t')\rho(r',t')d^3r'dt+\left(\frac{\partial p}{\partial T}\right)_\rho T(r,t), \tag{1.10}$$

$$\mu(r,t)-\mu_0=\int K(r-r',t-t')c(r',t')d^3r'dt'+\left(\frac{\partial \mu}{\partial T}\right)_{c,p} T(r,t)+\left(\frac{\partial \mu}{\partial p}\right)_{c,T} p(r,t). \tag{1.11}$$

The case of weak spatial dispersion and the absence of temporal dispersion corresponds to the well-known Ornstein-Zernike form of the kernels Q and K

$$Q(r-r')=\tfrac{1}{2}a\delta(r-r')+\tfrac{1}{2}\alpha\nabla_{r'};\quad Q(k)=\tfrac{1}{2}(a+\alpha k^2). \tag{1.12}$$

It is interesting that in the immediate vicinity of T_c, where the mean-field theory is unusable, we get, according to modern scaling theory, $Q(k)=\frac{1}{2}(a+\alpha k^{2-\eta})$, where $\eta \ll 1$ and $a\equiv(\partial p/\partial\rho)_T$ has a different dependence on $(T-T_c)$. In other words, the influence of all nonlinear terms in $\rho(r',t')$ which should appear in (1.10) amounts to a linear relation between p and ρ without changing the form of dispersion law (1.12), taking $\eta=0$.

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[1] In the two-dimensional case, $\overline{v(t)v(0)}\sim 1/t$, i.e., the integral over the correlation function which represents the kinetic coefficient has a logarithmic singularity. Thus the usual hydrodynamics does not exist in two dimensions. Keyes and Oppenheim (1973a) developed a bilinear hydrodynamics, i.e., they found equations for the different correlation functions. In particular, they calculated the ω-k dependent self-diffusion and Brownian diffusion coefficients (Keyes and Oppenheim, 1973b; Keyes, 1975). One of their results is that, for the case of three dimensions, spatial dispersion ($k\neq 0$) leads to an exponential decay of the velocity correlation function and the "tail" (1.9) disappears.

To complete the system of hydrodynamic equations (1.8), (1.10), and (1.11), it is necessary to add the explicit form of the momentum and heat fluxes, P_{ik} and q. The first terms of the series in powers of the gradients of the thermodynamical variables for the pure substance usually have the following form (Landau and Lifshitz, 1963):

$$P_{ik}=p(r,t)\delta_{ik}-2\eta(D_{ik}-\tfrac{1}{3}D_{\alpha\alpha}\delta_{ik})+\zeta D_{\alpha\alpha}\delta_{ik},$$
$$q=-\lambda\nabla T(r,t), \tag{1.13}$$

where η, ζ, and λ are the coefficients of shear and bulk viscosity and the thermal conductivity respectively, while D_{ik} is determined by (1.8).

In general, near the critical point we have to generalize Eqs. (1.13) by taking into account the possible spatial and temporal dispersion of the medium, similar to (1.10)–(1.11). For example, the second equation in (1.13) transforms into the following form:

$$q(r,t)=\int\lambda(r-r',t-t')\nabla T(r',t')d^3r'dt'. \tag{1.14}$$

When some characteristic length of the problem under consideration is of the order of ξ, a spatial dispersion appears. For example, the character of the particle motion as manifested in the diffusion constant is different for motion over distances comparable to ξ and over distances much larger than ξ. This nonlocal behavior of the coefficient of Brownian diffusion was found experimentally by Lyons *et al.* (1974).

In some special cases of processes with comparatively slow relaxation (chemical reactions, energy transfer to internal degrees of freedom, etc.) frequency-dependent transport coefficients have been used for a long time [see, for example, the dependence of the bulk viscosity on the frequency of the form $\zeta=\zeta_0(1-i\omega\tau)^{-1}$ (Landau and Lifshitz, 1963)]. Let us notice also the $\omega-k$ generalization of ordinary hydrodynamics by Kadanoff and Martin (1963) and others, when, for example, in the hydrodynamic formula for the correlation function $g_{\rho\rho}=(-i\omega+Dk^2)^{-1}$ they considered the self-diffusion coefficient as a function of ω and k, $D=D(\omega,k)$ and then tried to find such dependence in a self-consistent way. Thus the equation for the correlation function has the following form in a K-space:

$$\frac{\partial}{\partial t}g_{\rho\rho}(k,t)+\int_0^t d\tau D(k,\tau)k^2 g_{\rho\rho}(k,\tau)=0. \tag{1.15}$$

The non-Markovian behavior in Eqs. (1.14), (1.15) leads to very special hydrodynamic equations near the critical point.

The four aspects of the hydrodynamic approach, referred to above, concern the need to take into account the nonlinearity of the hydrodynamic equations and the effect of compressibility. In most cases, not too close to the critical point it is enough to consider only linear terms in hydrodynamic equations, but sometimes the nonlinearity is crucially important. An example of this latter situation is the pure hydrodynamic method of finding the relation between the singular part of the kinetic coefficients (if any) and the singularities of the thermodynamic quantities in the critical points (Gitterman and Gorodetskii, 1969).

The idea of obtaining the fluctuation contribution in the kinetic coefficients is as follows. The distribution of the fluctuations over the volume occupied by the fluid is homogeneous when external differences of velocity and temperature are absent. Therefore there are no fluxes of energy and momentum associated with the fluctuations. In the presence of an external field the distribution of fluctuations changes in space, and energy and momentum fluxes appear. Clearly we have to use nonlinear hydrodynamic equations, because in the linear approximation there is no coupling between the external gradients and thermal fluctuations.

The method described above leads to the same results as all other methods: mode–mode coupling theory (Kadanoff and Swift, 1968; Swift, 1968; Kawasaki, 1970a) dynamic scaling theory (Halperin *et al.*, 1974; Siggia *et. al.*, 1976), etc. The defect of this method consists in the assumption that the hydrodynamic description of the singular parts of the kinetic coefficients is valid in the critical region, while the advantages are in being able to perform all further calculation in the framework of hydrodynamics without any additional assumptions, unlike the other methods.

As regards compressibility, the inclusion of this effect is important as a rule near the critical point. It is worth pointing out that sometimes it is necessary to include the compressibility even far from the critical point where the fluid is practically incompressible. Thus for a Brownian particle with mass m and velocity v moving in a fluid, the theorem of equipartition of energy $m\overline{v^2}/2=k_BT/2$ is true only for a compressible fluid. For an incompressible fluid there is the effect of entrainment of the fluid and $(m+M)\overline{v^2}/2=k_BT/2$, where M is the "induced mass" of the fluid (Zwanzig and Bixon, 1975).

C. Outline

Let us give here more detailed information on the contents of the subsequent sections.

We shall start (Sec. II) from hydrostatics ($v=0$ in the hydrodynamic equations). Two problems of crucial importance in all experiments near the critical points will be discussed, namely, the establishment of equilibrium and the influence of inhomogeneities on all measurements near the critical points.

It has been known for many years that extremely long times are needed to attain equilibrium states of fluids near the critical point. Experimentalists were obliged to wait hours or, sometimes, even days to get reproducible experimental data. Many incorrect results were obtained in experiments with samples which did not attain the equilibrium state. What were they waiting for?

We shall consider in Sec. II.A the establishment of equilibrium on the molecular level without convective motion. One finds both from theoretical considerations and from comparison with experiment that it is the attainment of thermal equilibrium which is the longest part of the whole process. Let us mention here a few qualitative results following from the nonlinearity of the heat conductivity equation. All thermal disturbances dissipate as a kind of thermal wave, i.e., they have a finite velocity of propagation in the sample, in contradistinction to the usual diffusionlike solution of linear heat conduction equations. The small temperature differences persist for the longest time, and this time characterizes the slowing down of processes in the establishment of equilibrium as a whole near the critical point.

In Sec. II.B the influence of gravity on the thermodynamic properties of substances is discussed. This effect can be illustrated by the following well-known problem. Let us consider a column of ideal gas of height H in the presence of gravity. The specific heat, defined as the derivative with respect to temperature of the sum of the internal and the potential energy, is close to the specific heat at constant volume C_V for $H < RT/mg$ or to the specific heat at constant pressure C_p for $H > RT/mg$. Here m is the molecule mass, R is the gas constant, and g is the acceleration due to gravity. In this example, gravity effects become significant only for large H.

However, near the critical point because of the steep rise of compressibility (1.1) even a small change in pressure (due to the pressure of the upper layers on the lower) may bring about changes in densities of more than 10% in a vessel only 1 cm high. The hydrostatic effect thus exerts a considerable influence on all the measured properties of a one-component fluid near the critical point. Such an effect is also important in binary mixtures where, due to (1.2), gravity causes a variation of concentration with height (Gitterman and Voronel, 1965).

In Sec. II.B we shall discuss the relation between the specific heat C_V of the "ideal" system (with constant density) and the real system described by $\overline{C}_V$ which is an average over the sample. It turns out that for all known forms of equations of state $\overline{C}_V > C_V$, while the experimental results show $\overline{C}_V < C_V$ in some temperature interval. This contradiction, if it exists, can be useful in choosing the appropriate equation of state near the critical point.

In Sec. III three popular hydrodynamic problems are discussed, namely the sphere motion, cylinder oscillation, and disk rotation in a compressible viscous fluid. All these problems can be exploited to suggest new experimental methods near the critical point.

The force acting on a sphere moving in a fluid is very closely connected with the diffusion coefficient in Brownian motion (Sec. III.A). The latter is the motion of a large heavy particle through a dense solvent of small light molecules. It is interesting to mention that the results of the usual theory of Brownian motion are still valid when the difference between the radius of Brownian particle R and the size of solvent molecules is small (Edwards, 1970; Keyes and Oppenheim, 1973b, 1975). This not so clear question becomes even more difficult near the critical point where the new characteristic parameter ξ appears. In the vicinity of the critical point ξ increases [see Eqs. (1.4)] and various relations between ξ and R are possible. We shall discuss both $\xi < R$ and $\xi > R$. For $\xi < R$ the asymptotic Einstein–Stokes relation between coefficient of Brownian diffusion D and viscosity η is still valid for a compressible fluid in the linear approximation. Nonlinear corrections may change this result as the critical point is approached. Furthermore, for $\xi \gtrsim R$, D should decrease more slowly than $1/\eta$ (Keyes, 1975). On the other hand, for $\xi > R$ another source of stochasticity, different from the Langevin one appears (Gitterman *et al.*, 1970, 1978). The motion of the Brownian particle is governed by thermal density fluctuations with characteristic size ξ. The particle moves for some time inside a given fluctuation. After the decay of this fluctuation the particle is captured by another fluctuation and so on. The stochasticity of such Brownian motion is provided by the finite lifetime of the fluctuations and the randomness of their decay. For this "trapping" mechanism a sharp decrease of D towards the critical point was found.

The transversal oscillation of an infinite cylinder in a compressible viscous fluid will be discussed in Sec. III.B. For an incompressible fluid a similar problem was solved by Stokes 120 years ago. However, the first measurements near the critical point in the mixture aniline–cyclohexane (Ballaro *et al.*, 1971) showed the insufficiency of the Stokes approximation for the resistive force acting on the oscillating cylinder. The viscosity values calculated with the help of the Stokes formula coincide with independent calibration measurements in the region not too close to the critical point T_c, $(T - T_c)/T_c \gtrsim 10^{-4}$, but there is a clear discrepancy very close to the critical point, $10^{-6} \lesssim (T - T_c)/T_c \lesssim 10^{-4}$. Apart from the well-known Mach's number, another dimensionless small parameter can be formed, namely $(\frac{4}{3}\eta + \zeta)/c\rho R < 1$, where η and ζ are the shear and bulk viscosities, and R is the cylinder radius. The last inequality can be violated near the critical point, and the compressibility corrections to this parameter may be more important than corrections to Mach's number. The calculations described in Sec. III.B can be applied to the vibrating-wire viscometer (Tough *et al.*, 1964), which has some advantages for viscosity measurements near the critical point compared with other direct methods (capillary, falling sphere, rotating cylinder, oscillating disk). The latter methods have a series of defects associated with the increase of compressibility, hydrostatic effect, ease of phase separation due to the decrease of surface energy, and difficulties with thermal insulation. Furthermore, the vibrating-wire method has smaller hydrodynamic corrections (like end effects) than other methods.

The consideration of the third typical hydrodynamic problem, the rotation of an infinite flat disk in a compressible fluid, will be given in Sec. III.C. Tsechanskaya (1956) studied experimentally the dissolution of a disk of terephtatic acid rotating in a water–three-ethylamine mixture near the critical point. She found a sharp decrease in the convective diffusion coefficient as the critical point was approached. The theoretical approach to this problem consists of taking into account the finite depth of the fluid layer and the compressibility of a fluid and then finding the diffusion flow. It turns out that the finiteness of the layer is more important than the compressibility. A correction to the frictional force is found for an arbitrary relation between the height of the layer and the thickness of the boundary layer $(\eta/\rho\omega)^{1/2}$ where ω is frequency of the disk rotation.

Both homogeneous and inhomogeneous states can be realized depending on whether the experiment is performed immediately after the heating of the fluid or after the establishment of the hydrostatic effect. We shall give formulas for both cases.

In Sec. IV the theory of the onset of free convection and the distinguishing features of internal and surface gravity wave propagation near the critical point will be given.

Convective motion in a fluid heated from below is stimulated by its thermal expansion, while density variations due to hydrostatic pressure and dissipative processes taking place in a fluid in motion tend to return the fluid to its initial state.

Usually one analyzes the effect of only one of these two factors on the conditions for the onset of convection, leading to one of two criteria, that of Rayleigh or of Schwarzchild. When compressibility is taken into account, but the dissipative processes are neglected, one obtains for the onset of convection the Schwarzchild criterion:

$$(\nabla T)_{\text{ad}} \equiv g\rho\left(\frac{\partial T}{\partial p}\right)_{\rho}\left(1-\frac{C_V}{C_p}\right)\begin{cases} >\left(-\dfrac{dT}{dz}\right) & \text{no convection} \\ <\left(-\dfrac{dT}{dz}\right) & \text{convection} \end{cases} \tag{1.16}$$

where $(\nabla T)_{\text{ad}}$ is known as the adiabatic temperature gradient.

When compressibility is neglected but dissipative processes are taken into account, we are led to the Rayleigh criterion:

$$\frac{g\left(\dfrac{\partial\rho}{\partial T}\right)_{p} l^3(T_1-T_2)}{\nu\kappa}\begin{cases} <\gamma_0 & \text{no convection} \\ >\gamma_0 & \text{convection}. \end{cases} \tag{1.17}$$

Here $T_1 - T_2$ is the temperature difference across the layer of liquid of height l, and all other parameters in the left-hand side of (1.16) and (1.17) have their usual meaning. The critical Rayleigh number γ_0 depends on the boundary conditions.

Close to the critical point of pure fluids the compressibility increases sharply [see Eq. (1.1)] and the transport coefficients also increase. Consequently it is essential to consider both compressibility and dissipation in establishing criteria for the onset of convection (see Sec. IV.A) (Gitterman and Steinberg, 1970a, b).

The appearance of a nonstationary (oscillatory) instability in addition to the stationary, Bénard effect (which, as a matter of fact, is called free convection), is a significant distinction between compressible and incompressible fluids (Sec. IV.C) (Steinberg, 1971b).

It has been shown (Pellew and Southwell, 1940) that for an incompressible fluid only the stationary convective instability appears. However, the equations of convection for compressible fluids may also have complex eigenvalues, i.e., oscillatory convective instability is possible. It turned out that oscillatory convection may take place only in the immediate vicinity of the critical point. The density-relaxation mechanism, related to the bulk viscosity, is the new factor responsible for the new type of instability.

In Sec. IV.D the propagation of internal and surface gravity waves in a critical fluid will be discussed (Gitterman and Steinberg, 1972).

Internal gravity waves can be propagated as disturbances of an inhomogeneous fluid in mechanical equilibrium. The propagation of internal waves is closely related to stationary and oscillatory convective instabilities. Usually one considers internal waves in a fluid stratified by the gravity rather than by temperature fluids. There have been no investigations of the connection between internal waves and convective instability. In the compressible fluid both these phenomena are described by the same equations, as seen in Sec. IV.D.

The eigenvalues of these equations depend on the boundary conditions. When one of the boundaries or both are free, a new type of wave appears, namely, surface (or Rayleigh) waves. Such waves, as well as the gravity waves, propagating on the boundary surface between two compressible fluids, have some anomalies towards the critical point.

Finally, in Sec. V some conclusions will be given.

II. HYDROSTATICS

A. Thermal relaxation

The establishment of equilibrium in a fluid at rest near the critical point is an interesting and yet not fully understood problem.

It is natural to expect that equilibrium is established in two steps: first there is a relatively rapid smoothing of mechanical perturbations on a hydrodynamic level (lasting on the order of a minute) and then there is the slower process of establishment of total equilibrium on the molecular level (lasting hours and more) (Lorenzen, 1953; Palmer, 1954; Chaskin *et al.*, 1967; Dahl and Moldover, 1972; Brown and Meyer, 1973).

We consider here only the establishment of thermal equilibrium on the molecular level, given the equilibrium distribution of density (Gitterman and Steinberg, 1972a). The isothermal process by which the density reaches its equilibrium is a comparatively rapid one—theoretical considerations and comparison with experiment yield characteristic times of between 1 and 10 min for typical systems (Berestov and Malyshenko, 1970).

We shall show below that, in order to obtain reliable experimental data, one should eliminate temperature inhomogeneities induced by the inhomogeneity of the external temperature field, the different speeds of heat transfer from two phases in two-phase system, etc.

In cases where these temperature differences are unavoidable, for example, in steady-state measurements of thermal conductivity, one should wait long enough for an equilibrium distribution to be established. If this condition is not fulfilled, then by taking measurements during the establishment of the final temperature distribution, one may find thermal conductivities which differ from experiment to experiment.

The heat conduction equation governing the establishment of thermal equilibrium in a single-phase region has the usual form

$$\rho C_p\frac{\partial T}{\partial \tau} = \lambda\frac{\partial^2 T}{\sigma z^2} \tag{2.1}$$

where λ is the conductivity, τ the time, and z the vertical coordinate.

Equation (2.1) contains, as usual, the specific heat at constant pressure, since if one has a vertical density inhomogeneity, an equilibrium pressure is established at a given level more rapidly than the equilibrium density, by a factor equal to the ratio of the sound velocity to the velocity of a fluid element.

Near the critical point the establishment of thermal equilibrium depends on the density distribution, itself dependent on the temperature distribution. This means that the nonlinearity of Eq. (2.1) plays an essential role.

The dependence of the density ρ and specific heat C_p on height and temperature[2] are determined by the simultaneous solution of the two equations of hydrostatics, namely the Euler equation $dp = -\rho g dz$, and the equation of state near the critical point, $p = p(\rho, T)$.

Eliminating p from these two equations, one finds $\rho = \rho(T, z)$. C_p is found from thermodynamic relations. The resultant ρ and C_p are then substituted into Eq. (2.1). This means that the density distribution $\rho(z, T)$ at any instant of time τ is being thermodynamically adjusted as the temperature changes slowly, so that we can study the $\rho(z, T)$ dependence for an arbitrary temperature distribution $T(z, \tau)$.

The asymptotic form of the equation of state for the temperature close to the critical one can be written in the form

$$\left(\frac{\partial p_1}{\partial \rho_1}\right)_t \approx B\rho_1^{\delta-1}, \tag{2.2}$$

where the dimensionless parameters $t = (T - T_c)/T_c$, $\rho_1 = (\rho - \rho_c)/\rho_c$, and $p_1 = (p - p_c)/p_c$ characterize the distance from the critical point, and δ is the critical index equal to approximately 4.5, according to scaling theory and experiment.

Restrictions on the validity of (2.2) in certain situations is discussed by Gitterman and Malyshenko (1967) and Chalyi and Alechin (1970). These authors also derive the density distribution corresponding to Eq. (2.2):

$$\rho_1 = [(\delta/B)|h + c(t-a)|]^{1/\delta}\,\mathrm{sgn}[h + c(t-a)], \tag{2.3}$$

where the dimensionless height $h = (g\rho_c/p_c)z$ is reckoned upward from the level $\rho_1 = 0$, $t = a$, and $c = (\partial p_1/\partial t)_\rho$.

From the well-known thermodynamic relation $C_p \sim (\partial p/\partial\rho)^{-1}$ we obtain: $C_p = C_p^0(B\rho_1^{\delta-1})^{-1}$. Using these formulas together with (2.2) and (2.3) one can rewrite Eq. (2.1) as

$$\frac{\partial\varphi}{\partial\tau} = m\varphi^{\delta-1/\delta}\frac{\partial^2\varphi}{\partial h^2} \tag{2.4}$$

where $\varphi = (\delta/B)[h + c(t-a)]$ and $m = (\lambda B/\rho_c C_p^0)(g\rho_c/p_c)^2$.

If the critical level is inside the sample, then Eq. (2.4) is a degenerate quasilinear equation of the parabolic type. Such equations arise in certain other physical problems, e.g., in the study of radiative heat transfer, in the theory of electronic thermal conductivity in a plasma, and in filtration theory. For an infinite system this equation has a homogeneous solution of the thermal-wave type with a finite propagation velocity for the disturbances irrespective of the value of δ (Zel'dovich and Kompaneets, 1950). The thermal-wave solution of the nonlinear equation is quite different from solutions of linear equations. For linear heat transfer processes, changes in temperature on the boundary elicit an instantaneous response in the temperature of each part of the system. On the contrary, for processes which are governed by Eq. (2.4) heat is propagated with a finite velocity, i.e., any fluid element will have a delayed response to changes in the boundary temperature.

We are interested in the solution of the boundary-value problem with given temperature disturbance ΔT of a fluid layer of thickness l:

$$T = 0 \text{ at } \tau = 0, \quad T = \Delta T \text{ at } z = 0, \quad T = 0 \text{ at } z = l. \tag{2.5}$$

The characteristic times of establishment of equilibrium τ_0 have been calculated numerically. The results are as follows:

$$\tau_0 \approx (10\text{–}200)\text{hours at } \frac{\Delta T}{T_c l} \approx (10^{-5}\text{–}10^{-7})\ \mathrm{cm}^{-1}. \tag{2.6}$$

As the characteristic time τ_0 in (2.6) we adopt the time at which the deviation from the actual steady-state distribution does not exceed 10^{-4} °K.

These estimates of τ_0 are in accordance with those obtained for the establishment of equilibrium in calorimetric experiments (Chaskin *et al.*, 1967) and with the relaxation times obtained from the width of the central component of the Rayleigh-scattering spectrum evaluated at $\kappa \sim 1/l$.

A further general property of the nonlinear equation (2.4) is that the relaxation time τ_0 depends on the boundary conditions, in particular on the initial temperature difference ΔT. From the numerical calculation one finds $\tau_0 \sim (\Delta T)^{-2/\delta}$. This means that the small temperature inhomogeneities persist the longest and lead to relaxation times of the order of hours or more.

In some experiments the corresponding times were found to be relatively short (of the order of minutes). In these cases either there were actually no temperature differences or, more usually, the sensitivity of the method used to determine whether equilibrium had been established was not adequate. Evidence in favor of this explanation comes from the observation of short times for the establishment of equilibrium in the work of Bykov *et al.* (1971). However, their special devices (a stirrer and an isothermal cup) which eliminated large temperature differences, also eliminated these short times. Subsequently an extremely sensitive method, involving thermograms, detected longer times due to the persistent small temperature differences in the fluid.

Another example of the effect of temperature differences on the properties of a fluid near the critical point can be found in the experiment of Blagoi *et al.* (1970), although this work was done on the mixture CH_4–CF_4 and not a pure fluid. They found inhomogeneities in the concentration along the height of the sample. However, after further investigation it became clear that the concentration inhomogeneities were actually a consequence of small temperature differences of the order 10^{-2} deg/cm. In later work by the same authors (Blagoi *et al.*, 1971) the concentration differences indeed disappeared when special measures were taken to avoid temperature differences (so that $\Delta T/l < 5 \times 10^{-4}$ deg/cm). Meanwhile some investigators had referred to the results given in the first work, but took no notice of the later results.

This example demonstrates the need for eliminating temperature inhomogeneities to obtain reproducible data near T_c or, failing that, of waiting long enough for equilibrium distribution to be established.

To complete our consideration of the relaxation time

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[2] For simplicity we neglect here the change of heat conductivity coefficient compared with that of C_p [see, however, Eqs. (4.18) and (4.19) below].

problem let us discuss the measurements of thermal relaxation times near the critical point of ^{3}He (Dahl and Moldover, 1972; Brown and Meyer, 1972) which still have no explanation. These experiments found a strong dependence of τ_0, the relaxation time for given temperature difference, on the regions of the phase diagram. It turned out that τ_0 is very short (less than 3 sec) everywhere in the one-phase part of the phase diagram and, in general, large (100–1000 sec) in the two-phase region near the critical point. It is noteworthy that τ_0 is large below the coexistence temperature near the gas branch of the coexistence curve and small in the symmetric part of the phase diagram below the liquid branch of coexistence curve. A physically clear but probably not easily solvable problem in connection with thermal relaxation is the following: can one find the law of meniscus motion when the temperature changes from T_1 to T_2 and the initial and final densities are known from the Maxwell area rule? Is the increase of τ_0 connected with the small velocities of the meniscus or with its pendulumlike oscillations near the final state, or with something else?

B. Specific heat of inhomogeneous systems

The hydrostatic effect is one of the most important factors governing the outcome of measurements near the critical point. In fact, the critical point of the fluid is an isolated point on the $\rho-T$ phase diagram. This means that due to gravity, the critical conditions are realized at a temperature equal to the critical temperature only on the one level of the sample where the density has its critical value. Measurements carried out over a finite-height sample will average over different densities. At $T=T_c$ the density differences are over 10% for a vessel of height 1 cm, i.e., they are very important for all measurement near the critical point.

As our understanding of critical phenomena increases we describe them by new, more realistic equations of state. Comprehensive theories of the hydrostatic effect and its influence on measurements of all thermodynamic quantities have been developed for each form of the equation of state. The simplest example was given above in Eqs. (2.2), (2.3).

Baehr (1954) presented a theory based on the van der Waals equation of state. The considerations of Gitterman and Malyshenko (1967) and Berestov *et al.* (1969) were based on van der Waals' equation modified to allow for a divergent specific heat at constant volume. Numerical calculations of the hydrostatic effect were performed by Schmidt (1971) using the Vincentini-Missoni *et al.* (1969) empirical equation of state and by Hohenberg and Barmatz (1972) based on the parametric equation of state (Schofield *et al.*, 1969).

We refer the reader to the original articles for details and will be content to present only one example, concerning the behavior of C_V with and without gravity above the critical point of a pure fluid, i.e., for $T>T_c$.

Let the mean density in the vessel be equal to the critical density $\bar{\rho}=\rho_c$. Then the specific heat of the inhomogeneous system is obtained by averaging over the height h of the vessel the quantity (for details see Berestov *et al.*, 1969):

$$C_{V,\mathrm{inh}}=C_V(T,\rho)+\left(\frac{\partial S(T,\rho)}{\partial \rho}\right)_T\left(\frac{\partial \rho(T,h)}{\partial T}\right)_h . \qquad (2.7)$$

The averaging of the first term in (2.7) leads to a decrease in the value of the specific heat as compared to the "ideal" system (when $\rho=\rho_c$ in the whole fluid) and it is, in particular, the cause of the finiteness of the specific heat at $T=T_c$.

As we move away, but not too far, from $T=T_c$, the inhomogeneity in the density decreases, i.e., the averaging of the second term in (2.7), a term which is absent in the "ideal" case, makes a positive contribution to the measurable specific heat. Far from the critical point compressibility is small; therefore there is no difference between "ideal" (without gravity) and real systems. Thus, for the intermediate temperature region, we cannot, generally speaking, say beforehand whether the homogeneous or the inhomogeneous system will have the higher specific heat.

The explicit form of the second term on the right-hand side of Eq. (2.7) depends on the form of the equation of state near the critical point. Using the above-mentioned equations of state it was found (Berestov *et al.*, 1973) that in a fairly wide temperature interval near the critical point the specific heat in the gravitational field $(\bar{C}_V)_g$ is larger than the "ideal" specific heat (Fig. 2):

$$(\bar{C}_V)_g>(C_V)_{g=0}-\text{theory} . \qquad (2.8)$$

On the other hand, the experiments on ethane (Berestov *et al.*, 1973), argon (Chashkin *et al.*, 1967), and helium (Moldover, 1969) lead to a dependence opposite to that of (2.8), i.e., the presence of gravity always leads to a decrease in the specific heat (Fig. 2). The same conclusion is borne out by the experiments of Edwards *et al.* (1968) on xenon, if one chooses the critical temperature correctly (Berestov *et al.*, 1973).

The "ideality" of the system can apparently be achieved experimentally by decreasing the height of the vessel (Edwards *et al.*, 1968) or by introducing a stirring system (Chashkin *et al.*, 1967). Of course doing the

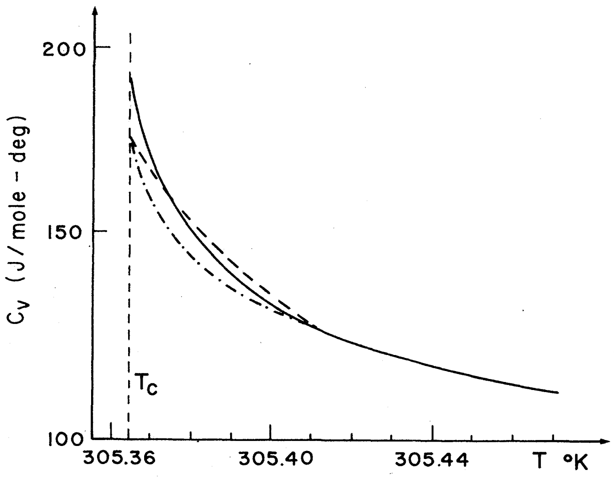

FIG. 2. The specific heat of a liquid near the critical point. The continuous curve corresponds to the experimental values of the "ideal" specific heat $(C_v)_{g=0}$ of ethane and the points represent the specific heat of ethane in the gravitational field.

experiment in outer space would achieve the same goal.

It is possible that further measurements of the specific heats of inhomogeneous and homogeneous fluids will turn out to be fundamentally important for establishing the equation of state of a fluid near the critical point.

III. SOME TYPICAL HYDRODYNAMIC PROBLEMS

A. Motion of a sphere in a compressible fluid: Brownian motion

Let us start from a well-known hydrodynamic problem, the resistive force acting on a sphere moving in a fluid. This problem is closely connected with the Brownian motion of a tagged body in the fluid in the following manner.

According to the basic assumption of the theory of Brownian motion, the force acting on the Brownian particle can be divided into a systematic part (friction η) and a random part. Thus the Langevin equation for the motion of a Brownian particle of mass M is[3]

$$M\ddot{x}+\eta\dot{x}=f_{\text{random}} \tag{3.1}$$

or in Fourier components

$$x_\omega=\alpha(\omega)f_\omega\,;\quad \alpha(\omega)=[-M\omega^2-i\omega\eta(\omega)]^{-1}\,. \tag{3.2}$$

Here we introduced the generalized susceptibility $\alpha(\omega)$, connected via the fluctuation-dissipation theorem with fluctuations of the quantity x. Thus it is easily shown (Leontovich, 1965; Gitterman and Gerzenstein, 1966) for the mean square displacement of the Brownian particle that

$$X^2(\tau)=\overline{[x(t)-x(t+\tau)]^2}=\frac{2k_BT}{\pi i}\int_{-\infty}^{\infty}\frac{\alpha(\omega)}{\omega}(1-\cos\omega\tau)d\omega\,. \tag{3.3}$$

Since $\alpha(\omega)$ is analytic, the integral (3.3) can be calculated as a contour integral.

The pole of the integrand in (3.3) at $\omega=0$ determines the asymptotic behavior and we then obtain the well-known Stokes–Einstein relation connecting the diffusion coefficient D, the mobility of Brownian particle b, and its radius R:

$$X^2(\tau)=2D\tau;\quad D=bk_BT;\quad b=(6\pi R\eta)^{-1}\,. \tag{3.4}$$

The poles of the function $\alpha(\omega)$ in Eq. (3.3) determine the characteristic times of nonstationary processes, which, in principle, can be found experimentally. Thus the problem of Brownian motion reduces to determining the function $\alpha(\omega)$ or according to (3.2), the function $\eta(\omega)$. For a macroscopic particle this reduces to a hydrodynamic problem of small-amplitude oscillations of a sphere about a fixed point in a compressible viscous fluid.

To solve the latter problem let us rewrite the system of hydrodynamic equations (1.8), (1.10), (1.12), and (1.13):

$$\rho_0\frac{\partial v}{\partial t}+\underline{\rho_0(v\nabla)}\,v=-\nabla p-\underline{\alpha\nabla\nabla^2\rho}+\eta\nabla^2v+\left(\frac{\eta}{3}+\zeta\right)\nabla\,\mathrm{div}v$$

$$\frac{\partial\rho}{\partial t}+\rho_0\,\mathrm{div}v+\underline{\mathrm{div}(\rho v)}=0;\quad \nabla p=c^2\nabla\rho\,. \tag{3.5}$$

For simplicity we omit here the equation of heat conduction. We consider its influence only in the choice of the corresponding square of the sound velocity c^2 in (3.5): either isothermal $c^2=c_T^2$ or adiabatic $c=c_s^2$, depending on the range of frequencies under consideration. In the case of asymptotic behavior ($\omega=0$) we must use c_T. In the correct terms [with characteristic frequency $\omega_0=c^2\rho_0/(\frac{4}{3}\eta+\zeta)$, see Eq. (3.9) below] the isothermal velocity c_T appears when the dissipative terms are large (Lukin *et al*., 1968), namely when

$$\kappa>\frac{\rho_0^2c_s^2\,\zeta\,R^2}{\frac{4}{3}\eta+C_v} \tag{3.6}$$

and $c=c_s$, when the inequality opposite to (3.6) is satisfied.

The boundary conditions for Eqs. (3.5) are of the form

$$v|_{r\to\infty}=0;\quad v|_{r=R}=U\equiv U_\omega e^{-i\omega t}\,. \tag{3.7}$$

The second boundary condition in (3.7) means that the fluid adheres perfectly to the surface of the sphere. Besides this "stick" limit, one can consider also the "slip" case, when the normal and tangential behavior of the fluid are specified separately (Zwanzig and Bixon, 1970). This leads to a change in the numerical factor in (3.4) from 6 to 4. The two nonlinear terms and the Ornstein–Zernicke fluctuation term are underlined in the system of Eqs. (3.5). To start with let us neglect these terms. Then the linear problem of the oscillation of the sphere in a compressible fluid can be solved (Gitterman and Gerzenstein, 1966; Zwanzig and Bixon, 1970; Chow and Hermans, 1973), and the function $\eta(\omega)$ in (3.2) has the following form:

$$\eta(\omega)=2\pi\eta R\,\frac{(1-y)(1-x+\frac{1}{3}x^2)+2(1-x)(1-\frac{1}{3}y-\frac{1}{3}y^2)}{(y^2/2x^2)(1-x)+(1-y+\frac{1}{2}y^2)} \tag{3.8}$$

where

$$x=i\left(\frac{\omega}{\omega_1}\right)^{1/2};\quad y=i\left(\frac{\beta\omega^2}{\omega_1(\omega-\omega_0)}\right)^{1/2};\quad \omega_0=-\frac{ic^2\rho_0}{\frac{4}{3}\eta+\zeta};$$

$$\omega_1=-\frac{i\eta}{\rho_0R^2};\quad \beta^{-1}=\frac{\zeta}{\eta}+\frac{4}{3}\,. \tag{3.9}$$

Neglect of compressibility ($y=0$) reduces Eq. (3.8) to the well-known Boussinesq approximation for an incompressible fluid. It turns out (Zwanzig and Bixon, 1970; Widom, 1971) that it suffices to take into account the ω dependence of the mobility $b(\omega)$ in the Boussinesq approximation [instead of the constant value $b=(6\pi R\eta)^{-1}$] in order to obtain from the hydrodynamic equations (3.5) the power rather than the exponential decay of the velocity correlation function (1.9).

On the other hand, the inclusion of the compressibility is crucially important for the initial rather than the asymptotic behavior of the velocity correlation function (see end of Sec. II.B above).

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[3] The influence of the long-time behavior of f_{random} on Eq. (3.1), which is similar to (1.9), was considered recently by Michaels and Oppenheim (1975).

Let us return to our problem of Brownian motion near the critical point. In experiments on Brownian motion it is in principle possible to measure both the asymptotic slope of the straight line $X^2(\tau)$ vs τ for $\tau \to \infty$ [see Eq. (3.4)] and the characteristic times of the nonstationary processes.

We see from Eq. (3.9) that two new characteristic hydrodynamic frequencies appear: $\omega_0 = -ic^2\rho_0/(\frac{4}{3}\eta + \zeta)$ and $\omega_1 = -i\eta/\rho_0 R^2$. Whereas ω_0 is determined only by the properties of the fluid, especially by $T - T_c$, the characteristic frequency ω_1 depends strongly on the size R of the Brownian particle. However, for R sufficiently small ω_1 is very high, and the correction to the asymptotic behavior of Brownian motion is determined completely by ω_0, i.e., by the properties of the fluid, and does not depend on the size and shape of the Brownian particle.

Then instead of the usual characteristic time [see Eq. (3.1)] $\tau \sim M/\eta$ which is of the order of 10^{-9} sec for $R = 10^{-5}$ cm, we get

$$\tau_0 \sim \frac{1}{|\omega_0|} = \frac{\frac{4}{3}\eta + \zeta}{c^2\rho} \sim (10^{-5} - 10^{-6}) \text{ sec at } \frac{T - T_c}{T_c} = 10^{-4} - 10^{-5} \ . \tag{3.10}$$

The characteristic time $\tau_1 \sim 1/|\omega_1|$ is rather small for the usual sizes of Brownian particles[4]: $R < \sqrt{\beta}\eta/\rho_0 c \sim (10^{-4} - 10^{-5})$ cm.

The force of resistance acting on the Brownian particle for $\omega \to 0$ depends on which of the conditions $\omega \gg |\omega_0|$ or $\omega \ll |\omega_0|$ holds.

Under normal conditions, i.e., for displacements of a Brownian particle during times larger than τ_0 (3.10), the resistive force has the Stokes value (3.4). Displacements during times smaller than τ_0 correspond to $y \sim i(\beta\omega/\omega_1)^{1/2} = \beta^{1/2}x$ in Eq. (3.8), i.e.,

$$\eta(\omega) = 6\pi R\eta_{\text{eff}} \text{ or } D = \frac{k_B T}{6\pi R\eta_{\text{eff}}} \ , \tag{3.11}$$

where

$$\eta_{\text{eff}} = \eta \frac{8\eta + 6\zeta}{11\eta + 6\zeta} \ . \tag{3.12}$$

Accordingly, Eq. (3.4) is changed by replacing η by η_{eff}, where $1 \geq \eta_{\text{eff}}/\eta \geq 0.7$.

Thus, within the framework of linear hydrodynamics, Brownian motion has no striking anomalies near the critical point. These conclusions are based on the assumption that there is no strong frequency dependence of the shear and bulk viscosities, at least for oscillation periods of the order of the displacement times of the Brownian particle which are of interest to us. Otherwise, new poles can appear in the integrand of Eq. (3.3).

We turn now to the influence of nonlinear and fluctuation effects on Brownian motion near the critical point. These effects are described by the underlined terms in Eqs. (3.5).

The magnitude of the convective nonlinear term $\rho_0(v\nabla)v$ in the Navier–Stokes equation relative to $\eta\nabla^2 v$ is determined by the dimensionless Reynolds number $\rho_0(v\nabla)v/\eta\nabla^2 v \sim \rho v R/\eta$, where $v = (k_B T/m)^{1/2}$. The Reynolds number is small for all usual sizes of Brownian particles. The first correction term to the Stokes formula (3.4) may be taken into account in the well-known Oseen approximation.

The nonlinear term $\operatorname{div}(\rho v)$ in the continuity equation in (3.5) was taken into account as a perturbation by Lukin *et al.* (1968) with the ratio ω_0^2/ω_1^2 [see Eq. (3.9)] as the small parameter. The inclusion of nonlinearity means physically that one considers the interference between the given motion of the particle (sphere oscillation in a compressible fluid) and its Brownian motion. It was found that nonlinearity leads to a decrease in mobility of the Brownian particle near the critical point:

$$b = \left\{6\pi\eta R\left[1 + \frac{k_B T_c}{2\pi c_T^2 \rho R^3} f\left(\frac{\eta}{\zeta}\right)\right]\right\}^{-1} ; \ f(1) \approx 0.2 \ . \tag{3.13}$$

The second term on the right-hand side of (3.13) is important only for small R ($R \sim 10^{-6}$ cm) and very close to the critical point $[(T - T_c)/T_c \sim 10^{-5} - 10^{-6}]$. For particles of given size R, Eq. (3.13) indicates proximity to the critical point when the decrease in mobility becomes important. However, Eq. (3.13) itself becomes inapplicable when the correction term becomes comparable to the Stokes term.

The system of Eqs. (3.5) also contains the Ornstein-Zernike fluctuation term, $\alpha\nabla\nabla^2\rho$, which we have so far neglected. This term describes weak spatial dispersion [see Eq. (1.12)]; its effect on the mobility of the Brownian particle was studied by Kozlov *et al.* (1968).

The fluctuation term increases the order of the system of hydrodynamic equations. Therefore one needs additional boundary conditions. In the work of Kozlov *et al.* (1968) such a condition was chosen in the form of the connection between the pressure and density on the surface of the particle

$$p_S(R) = \mathfrak{C}_S(R)\rho_S(R) \ , \tag{3.14}$$

where $p_S(R)$, $\rho_S(R)$, and $\mathfrak{C}_S(R)$ are the pressure, the density, and the compressibility on the particle surface, respectively. The fluid layer adjoining the surface of the particle is subject to surface forces. Therefore the conditions here are different from the critical ones, and $\mathfrak{C}_S(R)$ is of the order of the compressibility far from the critical point.

The calculation was done by perturbation theory in the small parameter ω_0^2/ω_1^2 [see Eq. (3.9)], and only terms involving the highest power of the bulk viscosity were taken into account. For the mobility of the Brownian particle Kozlov *et al.* found

$$b = \left\{6\pi\eta R\left[1 + \gamma\frac{k_B T}{\pi\rho R\alpha} \cdot \frac{4\eta + 3\zeta}{19\eta + 12\zeta}\right]\right\}^{-1} ; \ \gamma \approx 1 \ . \tag{3.15}$$

As may be seen from Eq. (3.15), the correction to the mobility of the Brownian particle remains finite at the

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[4] Apart from Brownian motion, other methods can also be utilized for studying characteristic times near the critical point, for example measurement of the spectrum of modulation of light or sound passing through the critical fluid, or measurement of the cross-susceptibility of a suspension of nonspherical conducting particles. These more direct methods give values of the characteristic times averaged over the sample, whereas the Brownian motion has a local character and therefore can be used also to study inhomogeneities near critical points.

critical point, as expected in an Ornstein-Zernike treatment.

All the results derived above for the one-component fluid carry over to binary mixtures by the substitution of

$$\frac{(\partial \mu/\partial c)_{p,T}}{(1/\rho)(\partial \rho/\partial c)^2_T}$$

for the sound velocity.

Brownian motion near the critical points of binary mixtures was studied by Keyes (1975) using bilinear hydrodynamics (Keyes and Oppenheim, 1973a, b; 1975). He found for the coefficient of diffusion in Brownian motion:

$$D=\frac{k_B T}{3\pi^2}\int_0^\infty \frac{dk}{\eta(k)}\chi^2(kR);$$

$$\chi^2(kR)=3\,\frac{\sin(kR)-(kR)\cos(kR)}{(kR)^3} \tag{3.16}$$

The cutoff function $\chi^2(kR)$ in (3.16) $[\chi(y)=1$ at $y=0$ and $\chi(y)\approx 0$ at $y\approx\pi]$ is the Fourier transform of the three-dimensional step function $\theta(r-r_1)$. The origin of this function is the finite radius of the Brownian particle, whose density is given by $n(r,t)=(\frac{4}{3}\pi R^3)^{-1}\theta[r-r_1(t)]$.

To find D from Eq. (3.16) we have to know the spatial dispersion of the viscosity $\eta=\eta(k)$ [cf. Eq. (1.14)]. This function was found by Kawasaki and Lo (1972)

$$\eta(k)=\eta(T)[1-F(k\xi)]\ , \tag{3.17}$$

where $\eta(T)$ is the thermodynamic viscosity, ξ is the correlation radius of the concentration fluctuations and $F(y)$ is the function tabulated by Kawasaki and Lo (1972), where $F(0)=0$; $F(10)=0.15$; $F(50)=0.29$, etc.

Substituting (3.17) in (3.16) one finds that the magnitude of the integral is determined by the relative value of the correlation radius ξ and the size of the Brownian particle R. Far from the critical point $R\gg\xi$ and Eq. (3.16) reduces to within an accuracy of $\frac{5}{6}$ (Keyes and Oppenheim, 1973a), to the Stokes-Einstein result (3.4).

Only in the immediate vicinity of the critical point, where $R\lesssim\xi$ does the function F in (3.17) become important and the coefficient of the Brownian motion (3.16) start to decrease more slowly than $1/\eta$.

In summary, Brownian diffusion slows down near the critical point. According to linear theory (3.4) the diffusion coefficient is proportional to $1/\eta$. As the critical point is approached the nonlinear corrections to this result become important and lead to a faster decrease of the coefficient of the Brownian diffusion [see Eq. (3.13)]. The asymptotic $(T\to T_c)$ behavior is then described in terms of a renormalized viscosity coefficient [see Eqs. (3.15) and (3.11)].

On the other hand, the inclusion of the spatial dispersion of the viscosity (3.17) leads to a slower decrease of D than $1/\eta$. This fact is important when the viscosity anomaly is obtained from Brownian motion experiments.

All the results mentioned above, apart from (3.16) and (3.17), are based on the Langevin equation (3.1). However, as the critical point is approached the correlation radius ξ increases and, in general, attains the size R of the Brownian particle. Naturally, in such a situation the usual conception of stochasticity does not work, because it is based on the assumption that the sphere must be large compared to the size of the fluid particles.

Nevertheless, another source of stochasticity can be found in this case (Gitterman, Likht, and Steinberg, 1970, 1978).

Let us assume that when $R<\xi$ the fluctuations carry the Brownian particle away and it moves some time together with the fluctuation. After the decay of the given fluctuation, which is a stochastic process, the Brownian particle moves independently in the medium with some friction till its capture by another fluctuation.

The simplest description of this process is the following. The Brownian particle executes two kinds of motion:

$$M\ddot{x}=-\beta_1 x \quad \text{free motion}\ , \tag{3.18}$$

$$M\ddot{x}=\beta(W-\dot{x}) \quad \text{motion with fluctuation}\ . \tag{3.19}$$

Here $\beta=6\pi\eta R$ and $\beta_1=6\pi\eta_1 R$ are the friction coefficients for the Brownian particle moving in the medium and inside the fluctuation, respectively, and W is the velocity of the fluctuations.

The usual case $R\gg\xi$ corresponds to considering only Eq. (3.18) with the random momentum $p_0=MU_0$ possessed by the particle at $t=t_0$. Einstein's relation (3.4) is obtained by averaging the solution of (3.18) over the initial conditions $(\overline{U}_0^2=k_B T/M)$.

When $R<\xi$ the particle moves primarily with the fluctuation [Eq. (3.19)] and one may neglect the motion between captures, i.e., Eq. (3.18) may be ignored altogether. Assuming the Maxwell distribution for the velocity of fluctuation one finds (Gitterman, Likht, and Steinberg, 1970)

$$D\sim k_B T\tau_1/12M_{f1}\ , \tag{3.20}$$

where M_{f1} is the "mass" of the fluctuation and τ_1 its lifetime.

The same result can be found by the microscopic approach (Gitterman *et al.*, 1978).

Thus we get formulas for the coefficient of Brownian diffusion D which are very different from those discussed above. Equation (3.20) contains a strong dependence on the proximity to the critical point determined by $M_{f1}\sim\xi^3$, as well as by τ_1 which is perhaps proportional to ξ. Finally

$$D\sim\xi^{-2}\sim[(T-T_c)/T_c)]^{4/3}. \tag{3.21}$$

Here we used $\xi\sim[(T-T_c)/T_c]^{-\nu}$, where $\nu=\frac{2}{3}$ is the critical index for ξ. Thus, for $R<\xi$, i.e., for a Brownian particle of sufficiently small size, and in the immediate vicinity of the critical point, one gets a sharp decrease of the coefficient of the Brownian diffusion as compared to the usual $1/\eta$ dependence.

Let us consider here a few experimental data concerning Brownian motion near the critical points of binary mixtures. There are three sets of data available: microphotography experiments on phenol–water (Baltsevich *et al.*, 1966) and on methanol–cyclohexane mixture (Martynets and Matizen, 1970), and autocorrelation spectroscopy measurements on the mixture nitroethane–isooctane (Lyons *et al.*, 1973, 1974).

Teflon microspheres of radius 3×10^{-5} cm were used as the Brownian particles by Lyons *et al.* (1974). These experiments were performed down to $(T-T_c)/T_c \gtrsim 3 \times 10^{-3}$. The reduction of the coefficient of Brownian diffusion D by 30% found in this experiment was connected with the parallel increase of viscosity η [see Eq. (3.4)].

This correlation between changes in D and η was not found in other experiments where the coefficient of Brownian motion decreased by half (Martynets and Matizen, 1970) or even by a factor of 4 (Baltsevich *et al.*, 1967).

In the work of Martynets and Matizen (1970) glass-dust particles of radius 2×10^{-5} cm were used in a mixture at temperatures T satisfying $(T-T_c)/T_c \gtrsim 3 \times 10^{-2}$. Under such conditions the correlation radius does not exceed 10% of the radius of the Brownian particles, and the mechanism of "trapping" of the particles by fluctuations [see Eqs. (3.18)–(3.20)] cannot yet appear (Lyons *et al.*, 1973).

On the other hand, in the experiments of Baltsevich *et al.* (1967) "accidental dust particles" of possibly smaller sizes were used. Estimates (Gitterman, Likht, and Steinberg, 1970) show that the "trapping" mechanism might possibly offer an explanation of their experiment.

B. Cylinder oscillation (Stoke's problem)

Finding the viscosity coefficients of a fluid by measuring the damping of the transverse oscillation of a wire in this fluid was a method suggested by Tough *et al.* (1964); subsequently it was applied to measurements near the critical point of binary mixtures by Ballaro *et al.* (1971) and to the superfluid transition by Bruschi *et al.* (1975).

The displacement from equilibrium of the cylindrical wire element $y(x,t)$, $(0 \leqslant x \leqslant l)$ is described by the following equation:

$$m_0 \frac{\partial^2 y}{\partial t^2} + \alpha_0 \frac{\partial y}{\partial t} = T \frac{\partial^2 y}{\partial x^2} + F \ . \tag{3.22}$$

Here m_0 is the mass per unit length, T is the tension and α_0 is the damping of oscillations in air. The function F determines the reaction of the fluid on the wire and can be written in the form

$$\frac{F}{\pi \rho R^2} = -\omega k' \frac{\partial y}{\partial t} - k \frac{\partial^2 y}{\partial t^2} \ . \tag{3.23}$$

Here R is the radius of the wire, ρ is the density of fluid, ω is the frequency of oscillation.

The problem is to connect theoretically the coefficients k and k', which characterize the induced mass and viscosity of the fluid, respectively, with the experimentally measured frequency and the friction coefficient of the oscillating wire.

The model description of this problem is the oscillation of an infinite cylinder, when the displacement is perpendicular to the cylinder axis. For an incompressible liquid this problem was solved by Stokes 120 years ago. He used linear hydrodynamic equations, which means that (Landau and Lifshitz, 1963)

$$\left(\frac{\nu}{\omega}\right)^{1/2} < R; \ l < R \ , \tag{3.24}$$

i.e., the oscillation amplitude l and the depth of the boundary layer $(\nu/\omega)^{1/2}$ are smaller than the radius of the cylinder R.

But near the critical point one has to take into account compressibility. The solution of the problem of the oscillation of a cylinder in a compressible liquid, in the linear approximation (3.24) (Gitterman, 1975), is similar to that of the problem of the motion of a sphere, used above in the analysis of Brownian motion. The results of the calculations are given in Fig. 3. The physical meaning of the parameters ϵ and τ is as follows. It is well known that compressibility can be neglected when Mach's number is small:

$$\epsilon = \frac{v}{c} = \frac{\omega R}{c} \ll 1. \tag{3.25}$$

However, this condition is insufficient in cases when dissipative processes are important. Then another di-

	K	K'
$\varepsilon < 1$	$(1 + 2\sqrt{2}y)(1 - \varepsilon^2 \ell n \varepsilon)$	$2\sqrt{2}y(1 - \varepsilon^2 \ell n \varepsilon) - \frac{\varepsilon^2}{2}$
$\varepsilon > 1$	$\frac{1}{\sqrt{2}} y(1 + \tau - \frac{2}{\varepsilon}) + \frac{\tau}{2}$	$\frac{1}{\sqrt{2}} y\ (1 + \tau - \frac{2}{\varepsilon}) + \frac{1}{\varepsilon}$
$\sqrt{\frac{\varepsilon}{\tau}} < 1$	$(1 + 2\sqrt{2}\ y)(1 + \frac{\varepsilon}{2\tau} \ell n \frac{\varepsilon}{\tau}) - \frac{\varepsilon}{2\tau}$	$2\sqrt{2}y\ (1 - \frac{\varepsilon}{2\tau}\ \ell n\ \frac{\varepsilon}{\tau})$
$\sqrt{\frac{\varepsilon}{\tau}} > 1$	$\frac{1}{\sqrt{2}}\ y\ (\ 1 - \frac{2}{\varepsilon\tau} \sqrt{\frac{\tau}{2\varepsilon}}) + \sqrt{\frac{\tau}{2\varepsilon}}$	$\frac{1}{2}\ y\ (1 + 4\sqrt{\frac{\tau}{2\varepsilon}}\ ) + \sqrt{\frac{\tau}{2\varepsilon}}$

FIG. 3. The results of the calculation of the coefficients K and K' connected with the induced mass and viscosity of fluid which moves because of cylinder oscillations.

$$\epsilon = \frac{\omega R}{c}; \ \tau = \frac{\frac{4}{3}\eta + \zeta}{\rho R c}; \ y = \left(\frac{\nu}{\omega}\right)^{1/2} \Big/ R \ .$$

mensionless parameter can be formed, and the possibility of neglecting the compressibility is conditional on the fulfillment not only of condition (3.25) but also of

$$\tau = (\tfrac{4}{3}\eta + \zeta)/c\rho R \ll 1 \ . \tag{3.26}$$

Near the critical point of pure fluids the volume viscosity can increase sharply, and in general condition (3.26) can be violated, although inequality (3.25) remains in force.

C. Disk rotation (Karman's problem)

The problem of the motion of an incompressible fluid caused by uniform rotation of an infinite flat disk with frequency ω was solved by Karman 55 years ago. It is possible to neglect boundary effects for a disk of finite radius R only if R is larger than the only length which may be formed from the fluid parameters, namely the thickness of the boundary layer, $(\nu/\omega)^{1/2}$ where ν is the dynamic viscosity. On the other hand, Karman considered only laminar flow which corresponds to a Reynolds number $\mathrm{Re} = \omega R^2/\nu$ less than the critical one $\mathrm{Re}_{\mathrm{cr}}$, which is of the order 10^5. Thus R may satisfy

$$\sqrt{\nu/\omega} < R < (\mathrm{Re}_{\mathrm{cr}})^{1/2}\sqrt{\nu/\omega} \ . \tag{3.27}$$

These inequalities can be rewritten as a limit on the rotation frequency of a disk of given radius,

$$\nu/R^2 < \omega < \mathrm{Re}_{\mathrm{cr}}\,\nu/R^2, \ \text{i.e. for } R = 1 \text{ cm:}$$

$$10^{-2}\ \mathrm{sec}^{-1} < \omega < 10^3\ \mathrm{sec}^{-1} \ . \tag{3.28}$$

Using the velocity profile in the fluid it is possible to find the moment M of the frictional forces acting on a disk or the drag coefficient $C_M = M/\frac{1}{2}\rho\omega^2 R^5$.

If the disk is made from soluble material its rotation leads to convective diffusion of its material. The convective diffusion problem has been studied by Levich (1962), who subdivided it into hydrodynamic and diffusion parts. First the velocity profile was found and then the concentration distribution was determined, using the given velocity profile. Such a simplification is justified owing to the usually low solubility of the disk material, i.e., the concentrations are small even for a saturated solution. The solubility can be characterized by the diffusion flow on the disk surface: $j = -D(\partial c/\partial z)_{z=0}$ where z is the vertical coordinate reckoned from the disk surface.

Measurements of j can be useful for finding the diffusion coefficient near critical points, and such an experiment has been carried out by Tsekhanskaya (1956).

In the critical region one is forced to consider Karman's problem for compressible fluid. In addition, because of the hydrostatic effect the liquid density increases with fluid depth, so it is necessary to consider a fluid of finite depth.

The problem for the finite-thickness layer cannot be solved exactly, and it is necessary to introduce the corresponding small parameter. If the depth of the layer H is more than the thickness of the boundary layer $(\nu/\omega)^{1/2}$, such a parameter is $(\nu/\omega)^{1/2}/H$. The solution is found as a series expansion for the boundary layer and for the rest of the fluid. The final solution is obtained by matching the expansions for the velocities and their derivatives at $z = (\nu/\omega)^{1/2}$. As a result we found corrections to Karman's solutions which are proportional to $(\nu/\omega)^{1/2}/H$ (Gitterman, unpublished).

In order to take into account the compressibility of the liquid we have to substitute into the hydrodynamic equations the density depending on the vertical coordinate z:

$$\rho = \bar{\rho} + \rho_0(z) + \rho_1(z) \ , \tag{3.29}$$

where $\rho_0(z)$ is the density variation in the stationary fluid (hydrostatic effect) (see Sec. II.B) and $\rho_1(z)$ is an additional density variation due to the fluid motion.

In the Karman problem the dimensionless hydrodynamic equations do not contain free parameters. In our case of compressible liquid in a finite layer we found two dimensionless parameters in the hydrodynamic equations: $(\partial\rho/\partial p)_T\omega\nu$ and $\omega^{3/2}\nu^{1/2}/g$.

Let us give here the results for two limiting cases: $\rho_0 \ll \rho_1$ and $\rho_0 \gg \rho_1$. Both these cases can be realized in experiments near the critical point. The first one $(\rho_0 \ll \rho_1)$ corresponds to an experiment which is carried out right after the heating of the fluid, while the hydrostatic effect is not yet established. The second case $(\rho_0 \gg \rho_1)$ is satisfied when the experiment starts after the establishment of the hydrostatic effect and when the frequency of disk rotation is not too high $(\omega \lesssim 400\ \mathrm{sec}^{-1})$.

The changes in the drag coefficients compared to the Karman case are

$$\rho_0 \ll \rho_1: \ \frac{C_M}{(C_M)_{\mathrm{Karman}}} \approx \left[1 + \frac{\omega\nu}{4}\left(\frac{\partial\rho}{\partial p}\right)_T\right]^{-1} \approx \left[1 + \frac{\omega(10^{-7})}{(T - T_c)/T_c}\right]^{-1} , \tag{3.30}$$

$$\rho_0 \gg \rho_1: \ \frac{C_M}{(C_M)_{\mathrm{Karman}}} \approx 1 + \overline{\left(\frac{\partial\rho}{\partial p}\right)_T} g\left(\frac{\nu}{\omega}\right)^{1/2} \begin{cases} \approx 1 + \dfrac{4\times 10^{-5}}{\omega^{1/2}(T - T_c)/T_c} \\ \approx 1 + 10^{-2}\omega^{-1/6} \end{cases} . \tag{3.31}$$

In Eqs. (3.30) and (3.31) the frequency ω is expressed in $(\mathrm{sec})^{-1}$ and the two cases in (3.31) correspond to temperature regions near T_c and in the immediate vicinity of T_c, respectively. The derivative $(\partial\rho/\partial p)_T$ in (3.31) is averaged over the boundary layer thickness $(\nu/\omega)^{1/2}$.

The correction to the diffusion flux $j_\infty \sim D^{2/3}\omega^{1/2}/\nu^{1/6}$ for the Karman problem is found as a series expansion in the parameter $(\nu/\omega)^{1/2}/H$ and in the above-mentioned two parameters characterizing the compressibility.

For thin layers $H \ll (\nu/\omega)^{1/2}$ we found a diffusion flow which turned out to be proportional to different powers of ν and ω and also depended on the depth of the fluid layer: $j \sim D^{2/3}\omega^{2/3}H^{1/3}/\nu^{1/3}$.

Comparing the influence of the finite height of the fluid layer and the influence of the compressibility on the hydrodynamics and the diffusion, one can see that the former factor is more important than the latter one.

IV. FREE CONVECTION, INTERNAL AND SURFACE GRAVITY WAVES

A. Onset of convection in compressible fluids

It is convenient to rewrite the system of hydrodynamic equations for compressible viscous and heat-conducting fluid by adding to the Navier–Stokes equation the gravity term:

$$\frac{\partial v}{\partial t} + (v\nabla)v = -\frac{\nabla p}{\rho} + gn + \nu\nabla^2 v + \left(\frac{\nu}{3} + \xi\right)\nabla\,\mathrm{div}v\ ,$$

$$\frac{\partial \rho}{\partial t} + \mathrm{div}(\rho v) = 0\ ;\ \ \rho T\left[\frac{\partial S}{\partial t} + (v\nabla)S\right] = \lambda\nabla^2 T + \mathfrak{C}'_{ik}\frac{\partial v_i}{\partial x_k}\ , \tag{4.1}$$

where n is a unit vector in the vertical direction (z axis).

We consider a layer of fluid at height l; the temperatures of the bottom and top are kept at T_1 and T_2, respectively.

Let us write the various thermodynamic parameters in (4.1) in the form

$$\rho = \bar\rho + \rho_0 + \rho';\ \ p = p_0 + p';\ \ T = \bar T + T_0 + T' \tag{4.2}$$

where $\bar\rho$ and $\bar T$ are the average density and temperature, and ρ_0, T_0, and p_0 relate to the distribution of these along the height, prior to the onset of convection, in the presence of gravity and the imposed temperature difference:

$$\nabla p_0 = (\bar\rho + \rho_0)g;\ \ \nabla T_0 = -An;$$

$$\frac{\partial \rho_0}{\partial z} = -\left(\frac{\partial \rho}{\partial p}\right)_T (\bar\rho + \rho_0)g - \left(\frac{\partial \rho}{\partial T}\right)_p A\ , \tag{4.3}$$

where $A = (T_1 - T_2)/l$.

Finally, the presence of convection [$v \neq 0$ in (4.1)] leads to small variations of pressure p', temperature T', and density ρ', which are related by the equation of state

$$\rho' = -(\bar\rho + \rho_0)\beta T' + \left(\frac{\partial \rho}{\partial p}\right)_T p'\ ;\ \ \beta \equiv -\frac{1}{\bar\rho + \rho_0}\left(\frac{\partial \rho}{\partial T}\right)_p\ . \tag{4.4}$$

Substituting (4.2)–(4.4) in Eqs. (4.1) we obtain the equations of convection. Since in the following only the onset of convection will be considered, we shall linearize these equations with respect to small p', T', and ρ'. We then obtain[5]:

$$\frac{\partial v}{\partial t} = -\frac{\nabla p'}{\bar\rho + \rho_0} + \nu\nabla^2 v - \frac{L_2 p' n}{(\bar\rho + \rho_0)l} + \frac{L_1 g T' n}{T_1 - T_2} + \left(\frac{\nu}{3} + \xi\right)\nabla\,\mathrm{div}v\ ,$$

$$\frac{L_1}{T_2 - T_1}\frac{\partial T'}{\partial t} - \frac{L_2}{(\bar\rho + \rho_0)lg}\frac{\partial p'}{\partial t} = \mathrm{div}v + \frac{(L_1 - L_2)vn}{l}\ , \tag{4.5}$$

$$\frac{\partial T'}{\partial t} - \left(\frac{\partial T}{\partial p}\right)_S \frac{\partial p'}{\partial t} = \kappa\nabla^2 T' + A(1 - \alpha)vn\ ,$$

where

$$\kappa = \frac{\lambda}{(\bar\rho + \rho_0)C_p}\ ;\ \ L_1 = \frac{T_2 - T_1}{\bar\rho + \rho_0}\left(\frac{\partial \rho}{\partial T}\right)_p\ ;$$

$$L_2 = lg\left(\frac{\partial \rho}{\partial p}\right)_T;\ \ \alpha = \frac{L_2}{L_1}\left(1 - \frac{C_v}{C_p}\right) \equiv \frac{(\nabla T)_{\mathrm{ad}}}{A} \tag{4.6}$$

and $(\nabla T)_{\mathrm{ad}}$ in (4.6) was defined in Eq. (1.16).

The system of Eq. (4.5) differs from the corresponding equations for an incompressible fluid by the presence of two dimensionless parameters. These are L_2, which is responsible for compressibility, and L_1, which is usually retained only in the "buoyancy force" term in the first of Eqs. (4.5).

Since according to Eq. (4.3) $\rho_0 = \rho_0(z)$, the coefficients in the system of Eqs. (4.5) are, in general, functions of the coordinates. However, it follows from Eq. (4.6) that

$$\rho = \bar\rho + \rho_0 \approx \bar\rho[1 + (L_1 - L_2)z/l]\ , \tag{4.7}$$

i.e., for $(L_1 - L_2) < 1$ (and arbitrary L_2) one can consider the coefficients in the system of Eqs. (4.5) as constants. Thereby we take into account only the first corrections with respect to $L_1 - L_2$ to the equations of free convection in an incompressible fluid. It is seen from Eqs. (4.6) and (1.1) that such an approximation becomes incorrect in the immediate vicinity of the critical point. We shall come back to this case later.

The solutions of (4.5) for $(L_1 - L_2) < 1$ depend on time as $e^{-i\omega t}$. If among acceptable values of ω there is at least one such that $\mathrm{Im}\omega > 0$, the fluid will become mechanically unstable, with the instability occurring at $\mathrm{Im}\omega = 0$. It was shown by Pellew and Southwell (1940) that in the case of an incompressible fluid ω is imaginary, hence the condition $\mathrm{Im}\omega = 0$ reduces to $\omega = 0$. This proof does not hold for the compressible fluid, and thus not only a stationary but also an oscillatory instability ($\mathrm{Re}\omega \neq 0$) can appear. The onset of oscillatory instability ("overstability") in a compressible fluid has been discussed in the astrophysical context (see the review article by Spiegel, 1972).

We shall come back later to oscillatory instability. Let us discuss now the onset of stationary convection. To do this, we need to omit all derivatives with respect to time from the system of Eqs. (4.5).

Eliminating pressure and horizontal velocity components from Eqs. (4.5) and assuming (by virtue of the infinite extent of the system in the horizontal direction) that dependence on horizontal coordinates is of the form

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[5] Jeffreys (1930) took compressibility into consideration in the equation for thermal conductivity, while Spiegel and Veronis (1960), Unno *et al*. (1960), Spiegel (1965), and Vickers (1971) analyzed these equations for a perfect gas.

e^{ikr} where k is the two-dimensional wave vector in the xy plane, we obtain for the amplitude of vertical velocity $v(z)$ and temperature $T'(z)$ the following equations:

$$\left\{l^4D^2+l^3L_1D\frac{d}{dz}+l^2L_2(L_1-L_2)\left[D+k^2\left(\frac{\xi}{\nu}+\frac{1}{3}\right)\right]\right\}v=\frac{\beta g l^4}{\nu}k^2T',$$
$$DT'=-(1-\alpha)\frac{A}{\kappa}v;\ D\equiv\frac{d^2}{dz^2}-k^2. \tag{4.8}$$

The boundary conditions for Eqs. (4.8) depend on whether the fluid layer is bounded by solid or free surfaces, i.e.,

$$v\big|_{z=\pm l/2}=0;\left(\frac{dv}{dz}+\frac{1}{\bar\rho+\rho_0}\frac{d\rho_0}{dz}v\right)\bigg|_{z=\pm l/2}=0;\ T'\big|_{z=\pm l/2}=0\ \text{ solid surfaces}$$

$$v\big|_{z=\pm l/2}=0;\left(\frac{d^2v}{dz^2}+\frac{1}{\bar\rho+\rho_0}\frac{d\rho_0}{dz}\frac{dv}{dz}\right)\bigg|_{z=\pm l/2}=0;\ T'\big|_{z=\pm l/2}=0\ \text{ free surfaces}$$

$$v\big|_{z=\pm l/2}=0;\left(\frac{dv}{dz}+\frac{1}{\bar\rho+\rho_0}\frac{d\rho_0}{dz}v\right)\bigg|_{z=-l/2}=0;\ \left(\frac{d^2v}{dz^2}+\frac{1}{\bar\rho+\rho_0}\frac{d\rho_0}{dz}\frac{dv}{dz}\right)\bigg|_{z=l/2}=0;\ T'\big|_{z=\pm l/2}=0\ \text{ the bottom surface is solid and the top is free} \tag{4.9a}$$

where the coordinate origin is halfway in the layer (Unno *et al.*, 1960; Spiegel, 1965; Vickers, 1971).

When the compressibility is small [cf. Eq. (4.7)] we come back to the boundary conditions for an incompressible fluid (Landau and Lifshitz, 1963):

$$v\big|_{z=\pm l/2}=0;\ \frac{dv}{dz}\bigg|_{z=\pm l/2}=0;\ T'\big|_{z=\pm l/2}=0\ \text{ solid surfaces}$$

$$v\big|_{z=\pm l/2}=0;\ \frac{d^2v}{dz^2}\bigg|_{z=\pm l/2}=0;\ T'\big|_{z=\pm l/2}=0\ \text{ free surfaces}$$

$$v\big|_{z=\pm l/2}=0;\ \frac{dv}{dz}\bigg|_{z=-l/2}=0;\ \frac{d^2v}{dz^2}\bigg|_{z=l/2}=0;\ T'\bigg|_{z=\pm l/2}=0\ \text{ the bottom surface is solid and the top is free} \tag{4.9b}$$

Equations (4.8) contain both criteria for the onset of convection, that of Schwarzchild (1.16) and that of Rayleigh (1.17). In fact, if compressibility is taken into account only in the heat conduction equation, while viscosity and thermal conductivity are neglected altogether, the condition $\nabla S=0$, or in accordance with (4.5) (for $\omega=0$) $\alpha=1$ will represent exactly the Schwarzschild criterion (1.16).

To obtain the second limiting case, that of the Rayleigh criterion (1.17), it is necessary to neglect compressibility in Eqs. (4.5), i.e., to put $L_2=0$, and of all the terms containing L_1 to keep only the "buoyancy force." Then Eqs. (4.8) take the usual form for an incompressible fluid:

$$D^2v=(\beta g/\nu)k^2T';\ DT'=-(A/\kappa)v\ . \tag{4.10}$$

From Eqs. (4.10) one can obtain a sixth-order equation with the Rayleigh number $R=\beta g A l^4/\nu\kappa$ as its eigenvalue, and kl as parameter. The function $R=R(kl)$ is defined by the boundary conditions (4.9b), and its minimum value represents the Rayleigh criterion (1.17). The values of γ in Eq. (1.17) are 657.511, 1707.726, and 1100.657 for the boundary conditions, (4.9b), respectively.[6]

In the case of a compressible fluid the system of Eqs. (4.8) is very cumbersome. The minimum eigenvalue is the characteristic temperature difference $(T_1-T_2)_c$ determining the onset of convection, and it now depends not only on the parameter kl, but also on L_1, L_2, as well as on the ratios of specific heats C_v/C_p and viscosity ξ/ν (for simplicity we shall assume that $\xi=\nu$). This not only makes an analytical solution impossible, but also presents considerable difficulties in a numerical treatment.

Because of this, a variational method (Jeffreys and Jeffreys, 1956) was used for obtaining an approximate solution of the problem of onset of free convection in a compressible fluid. Referring the reader for details to the original papers (Gitterman, and Steinberg, 1970a, b), we shall present here only the final result.

The dimensionless temperature difference (Rayleigh number) determining the onset of free convection is equal to

$$R=\gamma_0\frac{1+(l/l_1)^4+(l/l_1)^2(l_2/l_1)^2}{1+(l_3/l_1)^4(l_2/l)^2}\ , \tag{4.11}$$

where three lengths constructed from the parameters of the problem are introduced, namely,

$$l_1=\left[\gamma_0\nu\kappa/g^2\left(\frac{\partial\rho}{\partial p}\right)_T\left(1-\frac{C_v}{C_p}\right)\right]^{1/4};\ l_2=\left[\frac{\gamma_1\nu\kappa}{1-C_v/C_p}\left(\frac{\partial\rho}{\partial p}\right)_T\right]^{1/2};$$
$$l_3=\left[\frac{\gamma_0\nu\kappa}{g^2(\partial\rho/\partial p)_T}\right]^{1/4}. \tag{4.12}$$

The magnitudes of the numbers γ_c and γ_1 depend on the boundary conditions and change slightly with different

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[6] We note that for a superfluid solution the hydrodynamic equations are of still higher order. The number γ_0 for the free surfaces turns out to be the same as in a regular fluid, while for solid surfaces γ_0 proves to be approximately 7500. Thus the superfluid solution is much more stable with respect to the onset of free convection than the regular fluid.

choice of trial functions of the variational method. For solid surfaces using the simplified boundary conditions (4.9b): $\gamma_0 = 1707.8$ and $\gamma_1 = 70.5$.

Thus, comparison between the layer height l and parameters l_1, l_2, and l_3 enables one to get a criterion for the onset of convection from Eq. (4.11).

The numerical estimates for a "typical" fluid away from the critical point

$$[(\partial\rho/\partial p)_T \approx 10^{-10}\,\mathrm{sec}^2/\mathrm{cm}^2;\quad \nu \approx \kappa \approx 10^{-3}\,\mathrm{cm}^2/\mathrm{sec};\ 1 - C_v/C_p \approx 10^{-3}]$$

give

$$l_1 \approx 10\ \mathrm{cm};\ l_2 \approx 2\ \mathrm{cm};\ l_3 \approx 10^{-5}\ \mathrm{cm}\ .$$

It was found that for all the usually occurring layer heights the criterion for the onset of convective instability is the sum of the Schwarzchild and Rayleigh criteria with corrections depending on l. These two criteria are, obviously, limiting cases with respect to the parameter $(l/l_1)^4$: if $l^4 \gg l_1^4$ the height of the fluid layer is "large" and the Schwarzschild criterion is valid, while if $l^4 \ll l_1^4$ the height is "small" and it is necessary to use the Rayleigh criterion.

All the above is true for any compressible, viscous, and heat-conducting liquid. However, as the critical point is approached both the criterion for the onset of convection and the magnitude of parameter l_1 are changed. As the critical point is approached, $C_v/C_p \to 0$ and $l_1 \to l_3$. Hence one can rewrite the criterion (4.11) as

$$R = \gamma_0\left(\frac{l}{l_1}\right)^4 + \frac{\gamma_0}{1+(l_2/l)^2} = g^2\left(\frac{\partial\rho}{\partial p}\right)_T \frac{l^4}{\kappa\nu} + \frac{\gamma_0}{1+\gamma_1\nu\kappa(\partial\rho/\partial p)_T/l^2}\ . \tag{4.13}$$

The Rayleigh number R contains the factors C_p and β which increase towards the critical point. Therefore it seems convenient to rewrite Eq. (4.13), using the corresponding critical parameters as the scale for the imposed temperature difference $A = (T_1 - T_2)/l$:

$$b \equiv \frac{Ap_c}{g\rho_c T_c} = \frac{1}{c}\left\{1 + \frac{\gamma_0\nu\kappa}{g^2 l^4(\partial\rho/\partial p)_T[1+\gamma_1\nu\kappa(\partial\rho/\partial p)_T/l^2]}\right\} \tag{4.14}$$

where the dimensionless quantity $c = T_c/P_c(\partial p/\partial T)_c$ has no anomaly at the critical point.

The Schwarzschild criterion (1.6) in dimensionless variables has the form $b = 1/c$, i.e., it is satisfied at $T = T_c$. The second term on the right-hand side of Eq. (4.14) determines the corrections to the Schwarzschild criterion and decreases towards the critical point.

The approach towards the critical point changes the magnitude of the characteristic parameter l_1 (4.12) which divides the Schwarzschild and Rayleigh cases. Because of the increase in $(\partial\rho/\partial p)_T$ and C_p the value of l_1 decreases and equals approximately 0.1–0.01 cm at $(T - T_c)/T_c = (10^{-2}–10^{-4})$. Such values of l_1, in general, coincide with the distances between planes l in experiments measuring thermal conductivity close to the critical point. At $l \approx l_1$ it is wrong to use the Rayleigh criterion for an incompressible fluid to estimate the absence of convection in the experiment, as is sometimes done.

Free convection may distort results of measurements of different physical quantities, such as the specific heat. In fact, there is always some temperature difference inside a calorimeter. Let this difference be greater than the adiabatic temperature gradient contained in the Schwarzschild criterion (1.16). For example, for water $(\nabla T)_{\mathrm{ad}} = 4 \times 10^{-4}$ deg/cm. Then as the critical point is approached the temperature difference in the fluid will become, according to Eq. (4.14), the source of convective instability, which of course will distort the experimental results.

Now it is possible to trace the variation in stability of the liquid layer heated from below through the entire temperature range right up to the critical point (Fig. 4). At temperatures far from critical, the parameters of the fluid determining l_1, l_2, and l_3 are weakly dependent on temperature, and accordingly $[(T_1 - T_2)/l]_c$ is almost constant in a wide temperature interval (see the left part of the graphs in Fig. 4).

The limiting value of $[(T_1 - T_2)/l]_c$ in the immediate vicinity of the critical point is also known (see right half of Fig. 4). Here, according to (4.14) the Schwarzschild criterion is valid. In the immediate vicinity of the critical point, $C_v/C_p \ll 1$, and it ceases to depend on proximity to the critical point.

The transition from one limiting value to another, in other words, the change in stability of the fluid as the average temperature approaches the critical value, depends on the height of the fluid layer. For $l < l_1$ the approach to the critical point corresponds to a loss of stability, i.e., convection starts at the smaller temperature differences. For $l > l_1$ the stability increases.

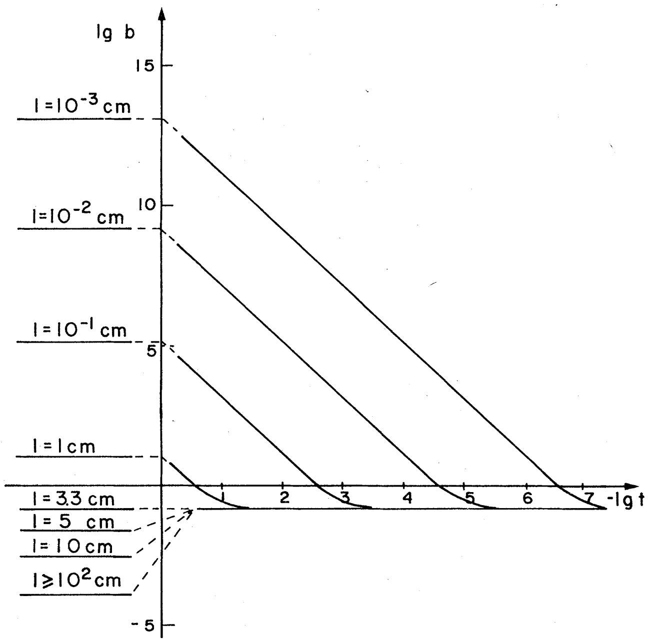

FIG. 4. Dimensionless critical temperature difference $b = (T_1 - T_2)_c P_c/l g \rho_c T_c$ determining the onset of convection as a function of the proximity to the critical point $t = (T - T_c)/T_c$ for different heights of the fluid layer.

B. Convection in a stratified fluid

Until now it was assumed that the density distribution with height is determined only by the generalized barometric formula (4.3) containing also the temperature difference. However, as discussed in Sec. II.B, the inhomogeneity of the fluid increases sharply close to the critical point. Therefore, the dependence $\rho_0(z)$ must be taken into account in calculating the criteria for the onset of free convection.

In analogy to Sec. II.B, the function relating density and height is found by the simultaneous solution of the Euler equation $dp = -(\bar{\rho}+\rho_0)g\,dz$, the thermal conductivity equation, and the equation of state. Equation (2.2) can be used as an asymptotic equation of state for temperatures close to the critical one. The common solution of these three equations has the following form:

$$\frac{\rho-\rho_c}{\rho_c} = \left\{\frac{\delta}{Bp_c}\left(\frac{\partial p}{\partial T}\right)_\rho (A - A_{\mathrm{ad}})|z - z_0|\right\}^{1/\delta} \operatorname{sgn}(z - z_0) \tag{4.15}$$

where z_0 is the level at which $\rho = \rho_c$.

In the immediate vicinity of the critical point, Eq. (4.15) should be substituted in Eqs. (4.5), and then by applying the variational method the characteristic temperature difference can be found.

Let us start from simple considerations leading to qualitatively correct results. Let us allow for compressibility only in the heat conduction equation. Then the temperature difference changes from A to $A(1-\alpha) = A - A_{\mathrm{ad}}$ [see (4.6)] and the solution becomes the same as for an incompressible fluid, with $A = (T_1 - T_2)/l$ in the Rayleigh criterion (1.17) replaced by $A - A_{\mathrm{ad}}$:

$$g\beta l^4 (A - A_{\mathrm{ad}})/\nu\kappa = \gamma_0 \,. \tag{4.16}$$

Without considering the hydrostatic effect we immediately get from (4.16) accurate to within the correction term $\gamma_1 \nu\kappa(\partial\rho/\partial p)_T/l^2$ the result (4.14) obtained previously.

However, close to the critical point the hydrostatic effect causes a substantial change in the conditions required for convection to start. In fact, a kind of self-consistency occurs here: the characteristic temperature difference, determining the start of convection, depends on the density distribution (4.15), which in turn is associated with the temperature difference. This is evidenced by the fact that $A - A_{\mathrm{ad}}$ enters criterion (4.16) both directly and through the other factors (β, κ, λ), which also depend on the density and hence, according to (4.15) on $A - A_{\mathrm{ad}}$.

We obtain for the coefficients in Eq. (4.5):

$$\beta \equiv -\frac{1}{\bar{\rho}+\rho_0}\left(\frac{\partial\rho}{\partial T}\right)_p \approx \frac{(\partial p/\partial T)_\rho}{\bar{\rho}+\rho_0}\left(\frac{\partial\rho}{\partial p}\right)_T ;$$

$$\kappa \equiv \frac{\lambda}{\rho C_p} = \frac{\lambda(\bar{\rho}+\rho_0)(\partial T/\partial p)_\rho^2}{T_c}\left(\frac{\partial\rho}{\partial p}\right)_T ;$$

$$\lambda \approx \lambda_0\left(\frac{p_c}{\rho_c}\right)^{1/2}\left(\frac{\partial\rho}{\partial p}\right)_T^{1/2} ; \nu \approx \nu_0 \,. \tag{4.17}$$

For λ in (4.17) we use the singularity given by dynamical scaling (Siggia *et al.*, 1976).

Substituting (2.2), (4.15), and (4.17) in (4.16), one may solve the resulting equation for A. The dependence on the vertical coordinate z appearing in this procedure is eliminated by using a suitable trial function in a variational calculation (Steinberg, 1971a). The only effect of all this is a numerical change $\gamma_0 \to \gamma_0'$.[7]

The hydrostatic effect has only this slight effect on the onset of free convection because, according to (4.15), the variation of density with height is small when the imposed temperature difference is close to the adiabatic temperature gradient. In other words, the change of the density with height due to temperature variation is almost completely compensated by the influence of the pressure variation on the density (Khait, 1969).

Finally one obtains for the dimensionless characteristic temperature difference $b \equiv Ap_c/g\rho_c T_c$ determining the onset of convection in the immediate vicinity of the critical point (with $\bar{\rho} \neq \rho_c$):

$$b = \frac{1}{c}\left[1 + \frac{p_c\left(\dfrac{T_c}{p_c}\right)^{2\delta/(\delta-3)}\left(\dfrac{\partial p}{\partial T}\right)_\rho^{4\delta/(\delta-3)} g^{(\delta+3)/(\delta-3)}}{\rho_c(\gamma_0'\lambda_0\nu_0)^{2\delta/(\delta-3)}B^{3/(\delta-3)}\delta^{3(\delta-1)/(\delta-3)}}\, l^{(5\delta+3)/(\delta-3)}\right]. \tag{4.18}$$

If in the temperature region under consideration the regular part of heat conductivity is larger than the singular one, i.e., we may put $\lambda = \lambda_{\mathrm{reg}} = \mathrm{const}$, (Sengers and Keyes, 1971), then in a similar way we obtain

$$b = \frac{1}{c}\left[1 + \frac{p_c\left(\dfrac{T_c}{p_c}\right)^{\delta/(\delta-2)}\left(\dfrac{\partial p}{\partial T}\right)^{2\delta/(\delta-2)} g^{2/(\delta-2)}}{\rho_c(\gamma_0'\lambda_0\nu_0)^{\delta/(\delta-2)}B^{2/(\delta-2)}\delta^{2(\delta-1)/(\delta-2)}}\, l^{2(\delta+1)/(\delta-2)}\right]. \tag{4.19}$$

Comparing (4.18) and (4.19) with (4.14), we find that the asymptotic estimate as the critical point is approached (the Schwarzchild criterion, Fig. 4) turns out to be true only at $l \to 0$. This result is physically reasonable, because due to the hydrostatic effect the critical conditions are realized only in a layer of zero thickness. Hence the inhomogeneity of the fluid causes an increase in stability with respect to the onset of convection.

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[7] Such a result is correct when the level with the critical density is located outside the fluid layer, i.e., $\bar{\rho} \neq \rho_c$. The case $\rho = \rho_c$ is more complicated (Steinberg, 1971a). Apart from changes in the criteria for the onset of convection, the very structure of the resulting convective motion will change. Two Bénard cells, one above the other, appear in the two-phase system. This conclusion about "two-flow" convection was obtained from the analysis of singularities of the exact eigenfunction of the convection equation including the hydrostatic effect. The possibility of a "two-flow" convection in a two-phase fluid was also noted by Busse and Schubert (1971). It would be interesting to check this result experimentally.

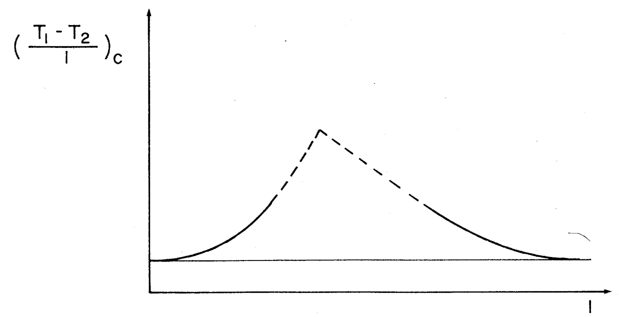

FIG. 5. Critical temperature difference

$$\left(\frac{T_1 - T_2}{l}\right)_c$$

determining the onset of convection as a function of the height of the fluid layer l.

The greater the height of the fluid layer l the earlier the hydrostatic effect becomes apparent. For example, for $l = 10^{-2}$ cm Eq. (4.15) and hence the criterion (4.18) or (4.19) becomes valid at $(T - T_c)/T_c \lesssim 10^{-4}$.

In summary, in the critical region, but not too close to the critical point, the criteria for the onset of convection are determined by Eq. (4.11) (Fig. 4). In the vicinity of the critical point criterion (4.14) is valid, which in turn, still nearer T_c goes over to the limit values (4.18) or (4.19), depending on the behavior of λ.

In the vicinity of the critical point the characteristic temperature difference determining the onset of convection is a nonmonotonic function of the height of the fluid layer l. Thus when the critical temperature is inside the layer and $\rho \neq \rho_c$, then as l decreases $[(T_1 - T_2)/l]_c$ increases from its initial adiabatic value as l^{-4} [see Eq. (4.14)]. Then, passing through the maximum [at $l \approx (10^{-1}$–$10)$ cm] the temperature difference increases at l^3 [Eq. (4.19)] or l^{17} [Eq. (4.18)] at $\delta = 4.5$, and finally it returns to the Schwarzchild criterion $b = 1/c$ (Fig. 5).

C. Oscillatory instability

There are many systems showing oscillatory convective instability. The appearance of an oscillatory branch in the instability spectrum is caused by a new relaxation mechanism additional to the temperature relaxation. For instance, this additional mechanism for a binary mixture is the relaxation of the concentration. For a layer of fluid in a transverse magnetic field, it is the relaxation of the magnetic moment, and so on.

In each of these cases the oscillatory instability starts only at a definite value of the parameter characterizing the additional relaxation mechanism. The corresponding parameters in the above examples are the dimensionless concentration difference and the critical magnetic moment (Hartman number).

In a compressible fluid a further oscillatory instability may occur caused by the density relaxation mechanism. This distinguishes it from the incompressible case, where only stationary instability is possible (Pellew and Southwell, 1940).

Let us consider the case when compressibility is important, i.e., when $L_2 = lg(\partial\rho/\partial p)_T > 1$ [see Eq. (4.6)]. This inequality holds if the fluid layer is deep

$$l > \left[g\left(\frac{\partial\rho}{\partial p}\right)_T\right]^{-1} \tag{4.20}$$

or near the critical point where compressibility (1.1) tends to infinity. We shall see below that additional conditions have to be fulfilled in order that oscillatory instability may occur, and that these conditions are met only near the critical point.

Let us now direct our attention to the system of Eq. (4.5). Analogously to our procedure in Sec. IV.B, we eliminate the pressure and the horizontal components of the velocity from (4.5) and assume a dependence e^{ikr} in the horizontal coordinates, where k is a two-dimensional wave vector in the horizontal x–y plane. Then we get a system of two equations for the amplitudes of the vertical velocity $v_z(z,t)$ and temperature $T'(z,t)$. We seek the solution of these equations in the form: $v_z(z,t) = f_1(z)\psi_1(t)$ and $T'(z,t) = f_2(z)\psi_2(t)$. Multiplying each of these two equations by $f_1(z)$ and $f_2(z)$, integrating over z from $-l/2$ to $l/2$, and assuming a t dependence of $e^{i\omega t}$, we get a system of two linear algebraic equations.

From the consistency condition we obtain the characteristic equation for ω:

$$\omega^4 + S_3\omega^3 + S_2\omega^2 + S_1\omega + S_0 = 0\,. \tag{4.21}$$

The formulas for the coefficients S_0, S_1, S_2, and S_3 are very cumbersome (Steinberg, 1971b) and are not discussed here. The stability conditions thus can be found from the analysis of the roots of Eq. (4.21).

The roots of the polynomial with real coefficients (4.21) occur in conjugate pairs. Therefore the onset of the oscillatory instability is characterized by the conditions $\mathrm{Re}\,\omega = 0$, $\mathrm{Im}\,\omega = \pm\omega_0$. On the other hand, one can write the conditions for the existence of a pair of purely imaginary roots in the form of certain relations between the coefficients S_0, S_1, S_2, and S_3 in (4.21).

The derived expression is extremely complicated in the general case. Therefore we introduce here the conditions for oscillatory instability for the case of free surfaces using the simplified boundary conditions (4.9b). The qualitative results are probably independent of the boundary conditions, only the numbers are expected to change. In fact, analysis shows (Vickers, 1971) that the Rayleigh numbers determining the onset of convection in a perfect gas are changed significantly on passing from boundary conditions (4.9b) to (4.9a).

It was found that apart from $L_2 > 1$ oscillatory instability requires the following conditions to be satisfied:

$$\frac{gl^3}{\nu\kappa} > L_2 \sim \frac{C_p}{C_v} \sim \frac{\nu}{\kappa} > 1\,. \tag{4.22}$$

These conditions are not generally met for an ordinary fluid, so there is no oscillatory convective instability there. But they are satisfied in a fluid near the critical point, as seen from the discussion in Sec. I.A.

It turns out that the characteristic dimensionless temperature difference determining the onset of oscillatory instability $b_0 \equiv Ap_c'/g\rho_c T_c$ and the frequency for the neutral oscillations are equal to

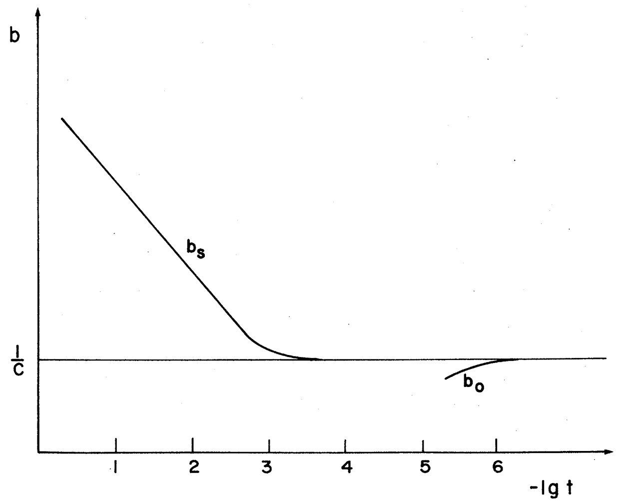

FIG. 6. Dimensionless temperature difference determining the onset of stationary (b_s) and oscillatory (b_0) convective instability as a function of proximity to the critical point at $l = 10^{-1}$ cm.

$$b_0 = \frac{1}{c}\left(1 - \frac{p_c^2}{(g\rho_c l)^2}\left(\frac{\partial p}{\partial \rho}\right)_T \pi^2\left\{\frac{\nu}{\kappa}\frac{C_v}{C_p} + \left[\left(\frac{\nu}{\kappa}\frac{C_p}{C_v}\right)^2 - 1\right]^{1/2}\right\}\right),$$

$$\omega_0^2 = \frac{g}{l}\frac{p_c}{\rho_c l g}\left(1 + \frac{2\nu C_v}{\kappa C_p}\right)^{-1}. \tag{4.23}$$

For typical values of critical parameters ($p_c = 50$ atm, $\rho_c = 0.5 g/\text{cm}^3$) we get $\omega_0 \approx 10^4/l$ Hz, i.e., for an l of 0.1 to 1 cm we get ω_0 of 10^4 to 10^5 Hz (acoustic frequencies). The physical reason for this instability is that there are vertical oscillations related to the sharp increase of the compressibility. Periodic density changes, in response to pressure change, result in a periodic variation in the buoyancy force when the thermal diffusivity is small.

Comparing now (4.23) with (4.11), (4.14), and (4.18) [or (4.19)] we see that near the critical point one reaches first the oscillatory convective instability. The quantity $(T_1 - T_2)_c$, which gives the criterion for oscillatory instability, increases towards the Schwarzschild criterion as the critical point is approached, while for stationary instability it tends to that limit from above (Fig. 6).

It would be interesting to check experimentally the appearance of these two types on instability in the immediate vicinity of the critical point when, with the increase of temperature difference, oscillatory convective instability develops first, and stationary convection appears only afterwards.

The onset of stationary as well as oscillatory instability near the critical point of binary mixtures has been obtained by Steinberg (1971c).

Unfortunately, almost all experiments concerning free convection and heat transfer near the critical point are performed in an engineering context. Substances in supercritical states are used in modern steam plants, as coolants for some nuclear reactors, etc. Therefore the subjects of these investigations are turbulent flow, the empirical connection between Reynolds and Nusselt numbers, and so on (Hall, 1971), and not the investigation of critical behavior.

D. Internal and surface gravity waves

Internal gravity waves (IGW) are bulk oscillations of the fluid propagating in mechanical equilibrium (i.e., in the absence of convection). The restoring force acting on a fluid element is proportional to the sum of contributions from the compressibility and heat expansion for the fluid heated from above, or to the difference of these effects for the fluid heated from below. In the latter case the temperature difference must be smaller than the characteristic temperature difference determining the onset of convection.

The IGW are described by the same system of Eqs. (4.5) as convection. Therefore, we obtain the same eigenvalue problem

$$f(\nabla T, \omega, k) = 0 \tag{4.24}$$

with boundary conditions (4.9). In Eq. (4.24) ω and k are the frequency and wave vector of the disturbance.

We have seen in Secs. IV.A–IV.C that with an extra condition on ω($\omega = 0$ for stationary and $\text{Im}\,\omega = 0$ for oscillatory convection) Eq. (4.24) gives a number of eigenvalues after minimization with respect to k. These are the characteristic temperature differences, and the smallest of them determines the onset of convection.

For the IGW, on the other hand, Eq. (4.24) serves as the dispersion equation for a given temperature difference ∇T. IGW occur above a characteristic frequency in (4.24).

Let us start from the simplest case, that of propagation of disturbances in a layer of an incompressible, viscous and heat conductive fluid. Here the change of the density is connected only with temperature changes. It has been found (Gitterman and Steinberg, 1972b) that IGW exist only if the temperature difference for heating from above is not too small, namely when the absolute value of the dimensionless temperature difference exceeds

$$R_{\text{IGW}} = 657.5 P_T\left(\frac{1 - P_T}{2P_T}\right)^2, \tag{4.25}$$

where $P_T = \nu/\kappa$ is the Prandtl number.

The result (4.25) was derived for the case of free surfaces. The criterion for the onset of convective instability in the fluid heated from below for the free surfaces is $R_{\text{conv}} = 657.5$.

Thus for $-R_{\text{IGW}} < R < R_{\text{conv}}$ the fluid is still mechanically stable (no convection) and IGW do not exist.

Let us consider now the vicinity of the critical point, where oscillatory as well as stationary convection appears. It is interesting to examine the relationship between conditions for the existence of IGW and for both types of convection.

Unfortunately, the fourth-order dispersion equation in ω (4.21) thus obtained is very cumbersome even for the simplest case of free boundaries. Since dissipation has an insignificant effect on the condition for the existence of IGW, we shall examine the phenomena in an ideal compressible fluid.

IGW in an ideal compressible fluid are described by the following system of equations (Gitterman and Steinberg, 1972b):

$$\frac{\partial v}{\partial t} = -\frac{1}{\rho_0}\nabla p' + \frac{g\beta\overline{T}}{C_p}S'n - \frac{g}{\rho_0 c_s^2}p'n\,,$$
$$\frac{1}{\rho_0 c_s^2}\frac{\partial p'}{\partial t} = \frac{g}{c_s^2}vn - \mathrm{div}v;\; \frac{\partial s'}{\partial t} = -\frac{dS_0}{dz}vn\,. \tag{4.26}$$

Here $c_s^2 \equiv (\partial p/\partial\rho)_S$ is the square of the adiabatic velocity of sound, $\overline{T}$ is the average temperature of the fluid, and S' and p' are the deviations entropy and pressure from equilibrium values produced by the disturbance.

It is usually assumed in the theory of IGW that the equilibrium gradients of entropy $\nabla S_0 = (dS_0/dz)n$ and density $\nabla\rho_0 = (d\rho_0/dz)n$ are vertical and constant. Their dependence on the vertical coordinate z is due to the gravitational field and the given temperature difference $\nabla T_0 = -An$, so that

$$\frac{dS_0}{dz} = -\frac{C_p}{T}A_0 + \beta g\,. \tag{4.27}$$

The dispersion relation for the system of Equations (4.26) has the form

$$\chi^2 = -k^2\left[\left(1-\frac{\omega_0^2}{\omega^2}\right)\left(1-\frac{\omega^2}{k^2c_s^2}\right) + \left(\frac{g}{c_s^2}+\frac{1}{2\rho_0}\frac{d\rho_0}{dz}\right)^2 k^{-2}\right]\,, \tag{4.28}$$

where k is the two-dimensional wave vector in the horizontal plane, and χ is determined from the equation for the eigenvalues for the particular cases. Thus, in the case of solid surfaces (4.9a),

$$\chi l = n\pi;\; n = 0, 1, 2, \ldots\,. \tag{4.29}$$

The expression for the limiting frequency ω_0 of the IGW in Eq. (4.28) has the form

$$\omega_0^2 = \frac{g\beta\overline{T}}{C_p}\frac{dS_0}{dz}\,. \tag{4.30}$$

This shows that the criterion for the existence of IGW is given by $dS_0/dz = 0$,[8] or, on account of (4.27), by the limiting temperature difference

$$A_0 = g\rho_0\left(\frac{\partial T}{\partial p}\right)_S\,, \tag{4.31}$$

which coincides with the Schwarzchild criterion (1.16).

As we showed in Sec. IV.B, the criterion for stationary convective instability also tends to the Schwarzchild condition as the critical point is approached, i.e., it coincides with the criterion for IGW. Sufficiently close to the critical point we also have oscillatory convection. Hence, as the imposed temperature difference increases we have a transition from IGW to oscillatory convection and then to stationary convection.

Equation (4.29) holds for solid surfaces. In the case of a solid lower boundary and a free upper boundary the equation for the eigenvalues will have the form:

$$tg\chi l = \chi l\omega^2\left[gk^2 l\left(1+\frac{\omega^2}{2gk^2\rho_0}\frac{d\rho_0}{dz}\right)\right]^{-1}\,. \tag{4.32}$$

This relation gives in the dispersion equation (4.28), along with the IGW and waves of an acoustic type, a surface wave. The latter wave corresponds to the single imaginary root of Eq. (4.32) with a dispersion law $\omega^2 = gkth(kl)$. One may analogously examine the surface wave propagating along the interface between two compressible fluids of densities ρ_1 and ρ_2 (Gitterman and Steinberg, 1972b). In this case the dispersion relation, containing acoustic, internal, and surface waves, is determined by the simultaneous solution of Eq. (4.28) for the upper and lower media and the following boundary condition at the interface:

$$\chi_1\rho_1 + \chi_2\rho_2 = (\rho_1-\rho_2)\frac{gk^2}{\omega^2}\,. \tag{4.33}$$

The presence of surface waves has been demonstrated by the experiments of Makarevich (1967), who observed the propagation of surface waves along the liquid–vapor interface of SF_6 in a horizontal test tube 20 cm long and 1 cm in diameter. Towards the critical point both the depth of penetration of the wave into the fluids and the velocity of propagation of the wave were seen to decrease.

These experimental results are in agreement with Eq. (4.3). In fact, for a given excitation frequency ω the densities ρ_1 and ρ_2 of coexisting liquid and vapor are brought closer together as the critical point is approached. According to Eq. (4.36), the wave vector k thus increases, and hence the penetration depth $1/k$ decreases; the wave narrows the interface. This was observed in experiment.

The observation of IGW and surface waves is likely to serve as a new method for detecting the critical parameters and indices of fluids.

On the other hand, they may also distort some experiments near the critical point. For example, in measurements of the thermal conductivity of fluids, thermal waves going vertically from a hot plane to a cold one can serve as a source for IGW propagating in the horizontal direction. The IGW will carry off some of the energy supplied to the boundary of a fluid and may lead to errors in the measurement of thermal conductivity. Although the amplitude of IGW is small, their characteristic frequency [cf. Eq. (4.30)] increases towards the critical point, so the energy carried off may be appreciable. It was found (Gitterman and Steinberg, 1970) that the error $\Delta\lambda$ in the thermal conductivity associated with excitation of an IGW is detected experimentally as a false maximum in the thermal conductivity: $\Delta\lambda/\lambda \sim \epsilon[(T-T_c)/T_c]^{-(3/2)\gamma}$, where $\epsilon \ll 1$ and $\gamma \approx \frac{4}{3}$ is the compressibility critical index.

V. CONCLUSIONS

The principal aim of this review has been twofold. First, we wished to emphasize the characteristic properties and possible applications of the hydrodynamics of fluids near a critical point. Secondly, we hoped to attract the attention of experimentalists to possible new

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[8] Note that for the nondissipative system we used the adiabatic compressibility. Therefore the criterion for the existence of IGW is determined by the gradient of entropy and not of density (Landau and Lifshitz, 1963).

methods in the experimental study of critical properties of substances.[9]

One can see from the above discussions that the hydrodynamics of critical fluids is very specific; it is neither ordinary hydrodynamics (compressibility is important) nor gasdynamics (the equation of state is not ideal). The system of hydrodynamic equations has coefficients increasing sharply towards the critical point, which leads to all the above-mentioned peculiar effects.

An interesting analogy to the behavior of critical fluids is the pretransitional phenomenon near points of hydrodynamic instability (transition from mechanical equilibrium to convective instability, transition from laminar to turbulent flow, etc.). One experimental verification of this analogy is a sharp increase in the linewidth of laser light scattered from Brownian particles suspended in a Poseuille laminar flow near the instability point (Goldstein and Hagen, 1967). Hydrodynamic instabilities take place for some value of R_c of a characteristic parameter, for example, the Rayleigh number (1.17) in the case of convective instability. The difference $R - R_c$ is analogous to $T - T_c$. Thermal fluctuations increase near R_c, the kinetic coefficients have some anomalies, and so on, showing a strong resemblance to a critical fluid. Let us note that the diffusion coefficient of Brownian motion diverges sharply [as $(R - R_c)^{-3/2}$] near a point of convective instability (Lekkerkerker and Boon, 1976). It is not clear why this theoretical result disagrees with calculations of the diffusion coefficient near the critical point (see Sec. III.A).

It is hoped that the above methods of investigating critical fluids may also be useful for studying hydrodynamic instabilities. On the other hand, experimental and theoretical study of the latter phenomena will help us to understand the breakdown of the validity of the approximations usually made in hydrodynamics.

In addition to the above-discussed methods of studying a critical fluid, we can mention another area of usefulness of hydrodynamics, namely the investigation of chemical reactions in fluids whose thermodynamic parameters are close to their critical values (Gitterman and Steinberg, 1975). Krichevski *et al.* (1961) found a slowing down of the rate of recombination of small numbers of iodine atoms into molecules in a solution of CO_2 near its critical point, and of chlorine atoms into ordinary molecular chlorine in a solution of CCl_2 near its critical point. These phenomena are probably conveniently considered as the hydrodynamic problem of the mobility of a foreign atom surrounded by solvent molecules (Leontovich, 1965).

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[9] There is also a wide field of application for the critical phenomena. As an example, let us mention the separation of mixtures, in particular isotopic mixtures. Appearance of a concentration gradient of components along the vessel height (hydrostatic effect—see Sec. II.B) represents a separation effect. Separating the fractions and then varying temperature and pressure in such a way as to remain on the critical curve, we can make the process of separation repetitive and continuous. Thus we can approach the critical point of the pure component along the critical liquid-vapor curve, i.e., we can separate the mixture completely.

In spite of the fact that a large amount of time is required in order to attain an equilibrium concentration distribution near the critical point, the basic part of this distribution is established relatively rapidly (see Sec. II.A). This initial stage proves to be sufficient for the effective separation of the mixture.

The small temperature gradient directed opposite to the gravity field could magnify the separation effect. Another way to increase the efficiency of separation is the centrifuging. Near the critical point there will be practically no diffusion which would impede the separation.

The concentration differences along the vessel height, say for isotopes, could be larger than the width of the two-phase region inside the coexistence curve. All this evidence indicates the advantages of the proposed method of the separation compared with other methods. The estimates of the efficiency of separation of He^3–He^4 mixture is overly optimistic (Gitterman and Voronel, 1965). The method should be particularly effective in the separation of heavy isotopes.

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