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## PRETRANSITIONAL EFFECTS NEAR THE CONVECTIVE INSTABILITY IN BINARY MIXTURES

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**Résumé.** — Les fluctuations prétransitionnelles sont obtenues dans le cas d'instabilité Rayleigh-Bénard pour un mélange binaire. Les résultats sont comparés avec ceux d'un fluide simple. Dans le système considéré les fluctuations de concentration sont amplifiées et bien que les fluctuations de vitesse augmentent de façon critique elles sont plus faibles d'un facteur d'ordre  $D/\chi$ . Le comportement du mode critique est comparé aux fluctuations du paramètre d'ordre obtenu par analyse classique de transition de phase. La région autour de l'instabilité où le traitement classique des fluctuations du paramètre d'ordre n'est pas valable est accrue d'un facteur  $(\chi/D)^{1/2}$  comparé à un fluide simple.

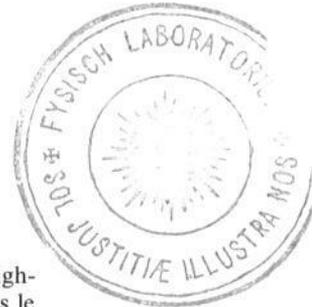
**Abstract.** — The pretransitional fluctuations of the Rayleigh-Bénard or convective instability are obtained for a binary mixture and compared to the one component case. There are now enhanced concentration fluctuations and although the velocity fluctuations are critically enhanced, they are weaker by a factor of  $D/\chi$ . The behaviour of the critical (soft) mode is compared to the fluctuations in the order parameter obtained for a classical analysis of a phase transition. The region around the instability where the classical treatment of the order parameter fluctuations is invalid is increased in the binary case by a factor of  $(\chi/D)^{1/2}$  over that of the pure fluid Rayleigh-Bénard instability.

**1. Introduction.** — Recently there has been a growing interest in pretransitional effects near hydrodynamic regime transitions [1]. It appears that these pretransitional effects bear a striking resemblance to those occurring near second order phase transition points. Indeed, the hydrodynamic fluctuations near hydrodynamic instability points show both a dramatic enhancement as well as a slowing down, the two most characteristic features of critical fluctuations near second order phase transition points.

The simplest example of a hydrodynamic instability is the Rayleigh-Bénard or convective instability [2] which occurs in a horizontal fluid layer heated from below. When the temperature gradient reaches a certain critical value stationary convection sets in spontaneously. The fundamental physical process that lies at the origin of this instability is the conversion of the energy released by the buoyancy force into the kinetic energy of the convective motion. Stationary convection sets in when the rate of energy transfer from the gravitational field begins to balance the rate of viscous dissipation of energy by the convective motion.

The convective instability in one-component systems has been studied for a long time but it is only during the last few years that the convective instability in binary mixtures has received attention [3]. The Rayleigh-Bénard instability in binary mixtures is of intrinsic interest because of the significant differences with the same instability in pure fluids. These differences are due to the concentration perturbations that decay very slowly compared to temperature perturbations. This leads to the possibility that one may have a convective instability even though the overall density gradient is not adverse, and under certain conditions, one may also find overstability rather than a simple exchange of stability, which is the only possibility for the convective instability in pure fluids. Perhaps the simplest situation is the case we study here, where the more dense component diffuses, due to the Soret effect, to the cold (upper) plate. In this instance one has only an exchange of stabilities.

In this paper we study the hydrodynamic fluctuations near the convective instability point in a binary mixture using stochastic hydrodynamic equations in a way similar to the study by Zaitsev and Shliomis [4]



of the pretransitional fluctuations in the Rayleigh-Bénard instability of the one component fluid. We obtain the concentration fluctuations, absent in the case of a one component fluid, and consider those features of the velocity fluctuations which are materially affected by the presence of the additional component.

In section 2 we present the linearized hydrodynamic equations describing the convective instability in binary mixtures, and consider the situation in which the concentration perturbation dominates.

In section 3 we include Langevin fluctuating forces in the hydrodynamic equations and derive, from the resulting set of stochastic differential equations, an equation for the branch of modes that become unstable near the transition point. The results are compared to those for the one component Rayleigh-Bénard problem.

In section 4 we discuss the analogies between pretransitional effects near second order phase transition points and near hydrodynamic regime transition points. We then compare the applicability of the classical theory to the treatment of the pretransitional region for the one and two component Rayleigh-Bénard instability. Finally, we briefly comment on the possibilities and limitations of the use of light scattering and Brownian motion to observe the critical behaviour of the fluid fluctuations near the instability point.

## 2. The Rayleigh-Bénard instability in binary mixtures. — 2.1 LINEARIZED HYDRODYNAMIC EQUATIONS. —

The steady state of the fluid in the stability region is characterized as follows : a linear downward directed temperature gradient is maintained steadily, the macroscopic fluid velocity is zero, the gravitational force is balanced by the hydrostatic pressure gradient and the thermal diffusion flow that results from the imposed temperature gradient is balanced by a concentration gradient. Labeling the steady state variables with a superscript *s* one has

$$T^s = T_0 - \beta z \quad (1a)$$

$$\mathbf{v}^s = 0 \quad (1b)$$

$$\nabla p^s = -g\rho^s \hat{\mathbf{n}} \quad (1c)$$

$$\nabla c^s = -\frac{k_T}{T_0} \nabla T^s. \quad (1d)$$

Here  $T_0$  denotes the value of the temperature at the reference position (taken here at the lower boundary  $z = 0$ ).  $\beta$  is the value of the temperature gradient,  $g$  is the gravitational constant,  $\hat{\mathbf{n}}$  is a unit vector pointing in the positive  $z$ -direction and  $k_T$  is the thermal diffusion ratio for which we neglect the variation with temperature. On the right hand side of eq. (1d) we have neglected the term that arises from barodiffusion, which, however, is small compared to the term arising from thermal diffusion.

Due to the imposed temperature gradient the fluid has uniaxial symmetry. In that case it is convenient [5] to use the following variables to describe the velocity field.

$$\text{div } \mathbf{v}, (\text{curl curl } \mathbf{v})_z, (\text{curl } \mathbf{v})_z.$$

For symmetry reasons  $(\text{curl } \mathbf{v})_z$  is not coupled to any of the other hydrodynamic variables. The remaining five hydrodynamic variables (two velocity and three thermodynamic variables) are coupled. These coupled equations lead to two sound modes and three diffusive modes. However, it can be argued [5] that the sound modes do not play a role in the convective instability and thus we may omit the variables corresponding to the sound modes i.e.  $\text{div } \mathbf{v}$  and pressure. Since  $\text{curl curl} = \text{grad div} - \nabla^2$ , it follows that if one omits  $\text{div } \mathbf{v}$  the variable  $(\text{curl curl } \mathbf{v})_z$  becomes  $-\nabla^2 w$  where  $w$  is the vertical component of the velocity. We then end up with the following coupled set of linearized equations [6]

$$\frac{\partial \nabla^2 w}{\partial t} = \nu \nabla^4 w - g\alpha_c \left( \frac{\partial^2 \gamma}{\partial x^2} + \frac{\partial^2 \gamma}{\partial y^2} \right) + g\alpha \left( \frac{\partial^2 \theta}{\partial x^2} + \frac{\partial^2 \theta}{\partial y^2} \right) \quad (2a)$$

$$\frac{\partial \theta}{\partial t} = \beta w + \chi \nabla^2 \theta \quad (2b)$$

$$\frac{\partial \gamma}{\partial t} = \frac{-k_T}{T_0} \beta w + D \nabla^2 \gamma. \quad (2c)$$

Here  $\theta$  is the perturbation in the steady state temperature,  $\gamma$  is the perturbation in the steady state concentration,

$$\alpha = \frac{-1}{\rho} \left( \frac{\partial \rho}{\partial T} \right)_{p,c}, \quad \alpha_c = \frac{1}{\rho} \left( \frac{\partial \rho}{\partial c} \right)_{p,T},$$

$\chi$  is the heat diffusion constant,  $\nu$  is the kinematic viscosity and  $D$  is the diffusion coefficient. In writing down eqs. (2a)-(2c) we have neglected the variation in the thermodynamic derivatives and transport coefficients due to the imposed temperature gradient. We have also neglected coupling, due to the Soret and Dufour effects, between concentration and temperature perturbations and retained only the coupling due to the imposed temperature gradient and the gravitational force between concentration and temperature perturbations on the one hand, and the velocity field on the other hand. Although only the vertical component  $w$  of the velocity appears in the equations, the horizontal components can be calculated easily from  $w$  [7]. Here we choose  $c$  to describe the concentration of the more dense component (i.e.,  $\alpha_c > 0$ ). As mentioned in the introduction, we restrict ourselves to the case where the more dense component diffuses to the cold plate, i.e. we consider mixtures for which the thermal diffusion ratio is

positive. For the sake of simplicity, we consider a fluid layer with hypothetical boundary conditions such that  $w$ ,  $\theta$  and  $\gamma$  can be written as

$$[w(\mathbf{r}, t), \theta(\mathbf{r}, t), \gamma(\mathbf{r}, t)] = \sum_{n=1}^{\infty} \int d\mathbf{\kappa} [w(n, \mathbf{\kappa}, t), \theta(n, \mathbf{\kappa}, t), \gamma(n, \mathbf{\kappa}, t)] \times \exp(i\mathbf{\kappa} \cdot \mathbf{x}) \sin\left(\frac{n\pi z}{d}\right). \quad (3)$$

Here  $\mathbf{\kappa} = (\kappa_x, \kappa_y)$  is the horizontal wave vector,  $\mathbf{x} = (x, y)$  is the horizontal position vector and  $d$  is the thickness of the fluid layer. Substituting eq. (3) in eqs. (2a)-(2c) one obtains the following equations for the Fourier components

$$\frac{\partial}{\partial t} \begin{bmatrix} w(n, \mathbf{\kappa}, t) \\ \theta(n, \mathbf{\kappa}, t) \\ \gamma(n, \mathbf{\kappa}, t) \end{bmatrix} = - \underline{M} \begin{bmatrix} w(n, \mathbf{\kappa}, t) \\ \theta(n, \mathbf{\kappa}, t) \\ \gamma(n, \mathbf{\kappa}, t) \end{bmatrix}. \quad (4)$$

Here the hydrodynamic matrix,  $\underline{M}$ , is given by

$$\underline{M} = \begin{bmatrix} \nu k^2 & -g\alpha\kappa^2 & +g\alpha_c\kappa^2 \\ -\beta & \chi k^2 & 0 \\ \frac{k_T\beta}{T_0} & 0 & Dk^2 \end{bmatrix} \quad (5)$$

where

$$k^2 = \kappa^2 + \left(\frac{n\pi}{d}\right)^2.$$

**2.2 STABILITY ANALYSIS.** — We now review the stability analysis of the set of coupled linear equations given in eq. (4) with the hydrodynamic matrix given by eq. (5). One can easily show that the only possibility for  $\underline{M}$  to have a negative root arises when the determinant of  $\underline{M}$  becomes smaller than zero. This means that the instability is reached when  $\det \underline{M} = 0$ , i.e.

$$D\chi\nu k^6 - g\alpha\beta\kappa^2(D + S\chi) = 0, \quad (6)$$

where

$$S = \frac{k_T}{T_0} \frac{\alpha_c}{\alpha}$$

is referred to as the Soret number. In the case we are considering  $S > 0$ . Introducing the Rayleigh number  $R = \frac{g\alpha\beta d^4}{\chi\nu}$ , it follows [8] that eq. (6) is satisfied for

$$R = \frac{k^6 d^4}{\kappa^2 \left(1 + \frac{S\chi}{D}\right)}.$$

The lowest value of  $R$  is

$$R_c = \frac{27\pi^4}{4} \frac{1}{\left(1 + \frac{S\chi}{D}\right)} \quad (7)$$

obtained for  $n = 1$  and  $|\mathbf{\kappa}| = |\mathbf{\kappa}_c| = \pi/\sqrt{2}d$ . This  $R_c$ , for the binary system, differs from that for the pure fluid by a factor  $(1 + S\chi/D)$  where  $S\chi/D$  is the contribution of perturbations in concentration relative to those of temperature. (The Soret number  $S$  provides the relative density, whereas  $\chi/D$  is a reflection of the relative efficiency of the concentration and temperature perturbations in utilizing the gravity field.) The critical Rayleigh number of eq. (7) is dependent on the fluid considered and to remove this a more appropriate form for  $R$ , for the system we are considering (i.e.  $S > 0$ ,  $\beta > 0$ ), would be

$$R = \frac{g\alpha\beta}{\nu} \left[ \frac{1}{\chi} + \frac{S}{D} \right].$$

Since, for a normal fluid,  $S$  is  $\simeq 5 \times 10^{-1}$  and  $\chi/D \simeq 10^2$  we find  $S\chi/D \simeq 5 \times 10$ ; and for our purposes we will consider that we may write  $S\chi/D \gg 1$ .

**3. Fluctuations near the instability point.** —

**3.1 STOCHASTIC HYDRODYNAMIC EQUATIONS.** — In order to study the fluid fluctuations we use a set of stochastic hydrodynamic equations that are obtained by adding fluctuating forces to the hydrodynamic equations describing the instability. We have

$$\frac{\partial}{\partial t} \begin{bmatrix} w(n, \mathbf{\kappa}, t) \\ \theta(n, \mathbf{\kappa}, t) \\ \gamma(n, \mathbf{\kappa}, t) \end{bmatrix} = - \underline{M} \begin{bmatrix} w(n, \mathbf{\kappa}, t) \\ \theta(n, \mathbf{\kappa}, t) \\ \gamma(n, \mathbf{\kappa}, t) \end{bmatrix} + \begin{bmatrix} F^{(w)}(n, \mathbf{\kappa}, t) \\ F^{(\theta)}(n, \mathbf{\kappa}, t) \\ F^{(\gamma)}(n, \mathbf{\kappa}, t) \end{bmatrix} \quad (8)$$

where

$$\langle F^{(\alpha)}(n, \mathbf{\kappa}, t) F^{(\alpha')}(n', \mathbf{\kappa}', t')^* \rangle = 2 Q^{(\alpha, \alpha')} \delta_{n, n'} \delta(\mathbf{\kappa} - \mathbf{\kappa}') \delta(t - t'); (\alpha, \alpha' = w, \gamma, \theta).$$

In this paper we assume that the intensities  $Q^{(\alpha, \alpha')}$  of the fluctuating forces remain regular near the instability point [we comment on this further in section 4]. Following the argument of Zaitsev and Shliomis [4], that the fluid remains locally in equilibrium and that therefore one can employ the equilibrium expressions for the intensities of the fluctuating forces, one obtains, using the fluctuation-dissipation theorem,

$$Q^{(w, w)} = \frac{1}{2} \frac{k_B T \chi^2}{\pi^2 d \rho k^2} \nu k^2 \quad (9a)$$

$$Q^{(\gamma, \gamma)} = \frac{1}{2} \frac{k_B T}{\pi^2 d} \frac{Dk^2}{\rho \left(\frac{\partial \mu}{\partial c}\right)_{p, T}} \quad (9b)$$

$$Q^{(\theta, \theta)} = \frac{1}{2} \frac{k_B T^2}{\pi^2 d} \frac{\chi k^2}{\rho c_p} \quad (9c)$$

where  $k_B$  is Boltzmann's constant,

$$\left(\frac{\partial\mu}{\partial c}\right)_{p,T} = \left(\frac{\partial[\mu_1 - \mu_2]}{\partial c_1}\right)_{p,T}$$

with  $\mu_1$  and  $\mu_2$  the chemical potentials per unit mass of species 1 (the more dense component) and species 2 and  $c_p$  is the specific heat at constant pressure.

3.2 THE UNSTABLE MODE. — The set of three coupled equations (8) have three eigen values  $\lambda_i(n, \kappa)$ ,  $i = 1, 2, 3$  for each wave vector  $\left(\kappa, \frac{n\pi}{d}\right)$ . To each of these eigen-values there corresponds an eigen mode  $u_i(n, \kappa, t)$ ,  $i = 1, 2, 3$ . Let  $\lambda_1(n, \kappa)$  [for a given wave vector  $(\kappa, n\pi/d)$ ] be the smallest eigen value. Then for  $R \rightarrow R_c$ ,  $\lambda_1(1, \kappa_c) \rightarrow 0$  and we refer to the eigen modes  $u_1(1, \kappa, t)$ , corresponding to the branch of eigen values  $\lambda_1(1, \kappa)$ , as the branch of unstable modes, we denote  $u_1(1, \kappa, t)$  by  $\psi(\kappa, t)$  and  $\lambda_1(1, \kappa)$  by  $\lambda_0(\kappa)$ . For  $\psi(\kappa, t)$  one can write the following equation

$$\frac{\partial}{\partial t} \psi(\kappa, t) = -\lambda_0(\kappa) \psi(\kappa, t) + F^\psi(\kappa, t) \quad (10)$$

where

$$\langle F^\psi(\kappa, t) F^\psi(\kappa', t')^* \rangle = 2 Q^\psi \delta(\kappa - \kappa') \delta(t - t'). \quad (11)$$

The mode  $\psi(\kappa, t)$  is a linear combination of  $w(1, \kappa, t)$ ,  $\theta(1, \kappa, t)$  and  $\gamma(1, \kappa, t)$ . For  $R = R_c$  and  $\kappa = \kappa_c$  the expansion coefficients (which can be expressed in terms of the eigen vectors of  $\underline{M}$ ) are given by simple expressions and since the eigen vectors of  $\underline{M}$  are smoothly varying functions of  $|\kappa - \kappa_c|$  and  $(R - R_c)$  we may use these expansion coefficients in the vicinity of that point as well and then we obtain

$$\psi(\kappa, t) = w(1, \kappa, t) + \frac{g\alpha\kappa_c^2}{\chi k_c^4} \theta(1, \kappa, t) - \frac{g\alpha_c \kappa_c^2}{Dk_c^4} \gamma(1, \kappa, t). \quad (12)$$

Similarly the intensity  $Q^\psi$  of the random force  $F^\psi$  can be written as a linear combination of  $Q^{(w,w)}$ ,  $Q^{(\theta,\theta)}$  and  $Q^{(\gamma,\gamma)}$ . Using eq. (12) one obtains

$$\begin{aligned} Q^\psi &= Q^{(w,w)} + \left(\frac{g\alpha\kappa_c^2}{\chi k_c^4}\right)^2 Q^{(\theta,\theta)} + \left(\frac{g\alpha_c \kappa_c^2}{Dk_c^4}\right)^2 Q^{(\gamma,\gamma)} \\ &= Q^{(w,w)} \left[ 1 + \frac{g\alpha T}{\beta c_p} \frac{D}{\chi S} + \frac{g\alpha_c T}{k_T \beta \left(\frac{\partial\mu}{\partial c}\right)_{p,T}} \right]. \quad (13) \end{aligned}$$

For typical liquids

$$\frac{g\alpha T}{\beta c_p} \frac{D}{\chi S} \sim 10^{-6}$$

and thus the contribution of the random force associated with the heat equation can be neglected; in general

$$\frac{g\alpha_c T}{k_T \beta \left(\frac{\partial\mu}{\partial c}\right)_{p,T}}$$

will also be smaller than 1. Thus, to a good approximation, we may set  $Q^\psi = Q^{(w,w)}$ , i.e. the dominant random force as far as the critical fluctuations are concerned is the random force associated with the velocity equation.

Close to the transition point the fluctuations in  $\psi$  are anomalously large and one can neglect all other fluctuations and mixed terms in comparison with the fluctuations in  $\psi$ . From eq. (10) one obtains

$$\langle \psi(\kappa, 0) \psi(\kappa', t)^* \rangle = \frac{Q^\psi}{\lambda_0(\kappa)} e^{-\lambda_0(\kappa)t} \delta(\kappa - \kappa'). \quad (14)$$

Expressing  $\gamma(1, \kappa, t)$  in terms of  $\psi(\kappa, t)$  one finds, close to the instability point, that

$$\begin{aligned} \langle \gamma(1, \kappa, t) \gamma(1, \kappa', t')^* \rangle &= \\ &= \frac{C^{(\gamma)}}{\lambda_0(\kappa)} e^{-\lambda_0(\kappa)|t-t'|} \delta(\kappa - \kappa'). \quad (15) \end{aligned}$$

We thus see that the concentration fluctuations show critical behaviour. Turning to the velocity fluctuations one obtains

$$\begin{aligned} \langle w(1, \kappa, t) w(1, \kappa', t')^* \rangle &= \\ &= \frac{C^{(w)}}{\lambda_0(\kappa)} e^{-\lambda_0(\kappa)|t-t'|} \delta(\kappa - \kappa') \quad (16) \end{aligned}$$

where

$$C^{(w)} = \left(\frac{D}{v}\right)^2 Q^{(w,w)}. \quad (17)$$

In order to compare this expression with the velocity fluctuations in the one component Bénard we expand  $\lambda_0(\kappa)$  in  $\varepsilon = (R_c - R)/R_c$  and  $\kappa - \kappa_c$ . One obtains, for the limit  $S\chi/D \gg 1$  and  $\chi \ll v$ ,

$$\lambda_0(\kappa) = \alpha \left[ \varepsilon + \frac{4(\kappa - \kappa_c)^2}{k_c^2} \right] \quad (18)$$

where

$$\alpha = Dk_c^2. \quad (19)$$

The expressions for the velocity fluctuations and for the  $\lambda_0(\kappa)$  obtained in the neighbourhood of the Rayleigh-Bénard instability for the one component fluid are the same form as those of eqs. (16) and (18) where now, in the limit  $\chi \ll v$ , one has [9]

$$C^{(w)} = \left(\frac{\chi}{v}\right)^2 Q^{(w,w)} \quad (20)$$

and

$$\alpha = \chi k_c^2. \quad (21)$$

Since both  $C^{(w)}$  and  $\alpha$  are different here we see that the velocity fluctuations for the same values of  $\varepsilon$  and  $(\mathbf{\kappa} - \mathbf{\kappa}_c)$  are, in the binary mixture, weaker by a factor of  $D/\chi \simeq 10^{-2}$ .

**4. Discussion.** — **4.1 ANALOGY TO SECOND ORDER PHASE TRANSITIONS** (cf. Ref. [1a]). — The pretransitional region of a second order phase transition of the instability type [10] is characterized by two well known effects : the fluctuations in the order parameter become large ; and they decay slowly. The free energy takes the familiar Landau-Ginzburg form [11]

$$F = F_0 + \frac{1}{2} \int d\mathbf{r} [a' \varepsilon (\eta(\mathbf{r}))^2 + \delta (\nabla \eta(\mathbf{r}))^2] \quad (22)$$

where  $\eta$  is the order parameter and  $\varepsilon = (T - T_c)/T_c$ . For the susceptibility

$$\chi_\eta = \left( \frac{\partial^2 F}{\partial \eta^2} \right)_T^{-1}$$

one obtains for the  $k$ th spatial fourier component, the result

$$\chi_\eta(\mathbf{k}) = \frac{1}{(2\pi)^3} \frac{1}{a' \varepsilon + \delta k^2} \quad (23)$$

which diverges as  $T \rightarrow T_c$  and the wave vector  $\mathbf{k}$  goes to zero. Employing the free energy of eq. (22) in the Einstein formulation for the equilibrium distribution function one finds the mean square fluctuation as

$$\langle |\eta(\mathbf{k})|^2 \rangle \sim k_B T \chi_\eta(\mathbf{k}).$$

Since  $\chi_\eta(\mathbf{k})$  diverges as  $\varepsilon$  and  $k$  go to zero the mean square fluctuation becomes large at the approach to the phase transition.

The relaxation time,  $1/\lambda_\eta$ , of the order parameter fluctuations can be extracted from these equilibrium results by employing the well known Van Hove result [12]

$$\lambda_\eta = \frac{L}{\chi_\eta} \quad (24)$$

where  $L$  is the so-called kinetic coefficient. Then using eq. (23) one obtains, directly, that

$$\lambda_\eta = L(2\pi)^3 [a' \varepsilon + \delta k^2]. \quad (25)$$

Assuming  $L$  is regular it is clear that as  $\varepsilon$  and  $k$  go to zero at the phase transition, the decay constant  $\lambda_\eta \rightarrow 0$ , a result referred to as *critical slowing down*.

Turning now to the hydrodynamic transition of the Bénard instability we begin by recalling that, as the instability is approached, the critical eigenvalue  $\lambda_0$  (eq. (18)) goes to zero so the decay of fluctuations in the critical (soft) mode is certainly slowed (i.e. we have

*critical slowing down*). Further the mean square fluctuation in the critical mode can be obtained from eq. (14) as

$$\langle |\psi(\mathbf{\kappa})|^2 \rangle \sim Q^\psi / \lambda_0(\varkappa). \quad (26)$$

Hence, assuming  $Q^\psi$  is regular [12], as  $\lambda_0(\varkappa) \rightarrow 0$  the mean square fluctuations of the critical mode will diverge as the instability is approached. In view of the very clear analogy between the behaviour of the critical mode at the instability and the order parameter at the phase transition we equate the critical mode to the order parameter for the hydrodynamic regime transition.

In addition, the form of the critical eigenvalue  $\lambda_0(\varkappa)$ , in the neighbourhood of the instability, is exactly the same, in terms of  $\varepsilon$  and  $\mathbf{\kappa} - \mathbf{\kappa}_c$  as that of the damping factor of the order parameter in the neighbourhood of the phase transition.

**4.2 LIMITATION TO THE CLASSICAL TREATMENT OF CRITICAL FLUCTUATIONS.** — The use of a linear Langevin equation or its compliment [13], the distribution function employing the Landau-Ginzburg form (Eq. 22) of the free energy, assumes that higher order terms do not play a significant role in the description of the pretransitional fluctuations of phase transitions. Ginzburg [14] provided a bound for this *classical* critical region by requiring, for the ordered regime, that the mean square fluctuations in the order parameter be much less than the square of the order parameter itself. A similar bound is obtained in the disordered regime by comparing fluctuations of second and higher orders [15].

We extend the Ginzburg criteria to hydrodynamic transitions and calculate a bound for the *classical* regime by requiring that in the ordered phase the mean square fluctuation in the critical mode be much less than the square of the critical mode. We assume that in the ordered regime the amplified mode, just past the instability, is the critical mode obtained from the linear treatment of the pretransitional region.

Following Chandrasekhar [16] one calculates the amplitude of the mode in the ordered phase by recourse to the non-linear hydrodynamic equations. Thus one obtains, for the one component Bénard, that the modulus squared of  $w(1, \mathbf{\kappa}_c)$ , the leading term in the critical mode, goes as

$$|\langle w(1, \mathbf{\kappa}_c) \rangle|^2 = C \left( \frac{\chi}{d} \right)^2 |\varepsilon|. \quad (27)$$

A similar procedure for the ordered phase in the binary Bénard, again assuming the  $\chi S/D \gg 1$ , gives

$$|\langle w(1, \mathbf{\kappa}_c) \rangle|^2 = C \left( \frac{D}{d} \right)^2 |\varepsilon| \quad (28)$$

where  $C$  is a constant of order  $10^2$  whose specific value depends on the geometry of the system.

The mean square fluctuation for the ordered phase may be related, simply (a factor of  $\frac{1}{2}$ ) to that for the disordered, i.e. pretransitional, phase, and we have

$$\langle |\delta w(1, \kappa)|^2 \rangle = \frac{C^{(w)}}{2 \lambda_0(\kappa)} \quad (29)$$

where  $C^{(w)}$  and  $\lambda_0(\kappa)$  are defined, for the two and one component cases, by eqs. (17) to (21). Taking the  $Q^{(w,w)}$  appearing in eqs. (17) and (20) to be for a volume  $d^3$  (i.e.  $Q^{(w,w)}$  is given by  $16 \pi^2/d^2$  times  $Q^{(w,w)}$  of eq. (9a)) we find, for the Ginzburg criteria for the one component case

$$|\varepsilon| \gg \left[ \frac{k_B T}{\chi \nu \rho d} \right]^{1/2}, \quad (30)$$

and for the binary mixture

$$|\varepsilon| \gg \left[ \frac{k_B T}{D \nu \rho d} \right]^{1/2}. \quad (31)$$

Since  $\chi \gg D$  it is clear that the lower bound for  $\varepsilon$  is larger in the two component case. Inserting values of  $\rho$ ,  $D$ ,  $\nu$ , etc., appropriate to a normal fluid, into eqs. (30) and (31) and taking  $d \simeq 1$  cm one finds, for the one component case the bound  $\varepsilon \gg 10^{-4}$  and for the binary mixture  $\varepsilon \gg 10^{-3}$ . Although the non-linear region in both cases is rather small non-classical effects could be more accessible in the binary mixture.

**4.3 EXPERIMENTAL CONSIDERATIONS.** — Two fundamental methods to probe fluid fluctuations are light scattering and Brownian motion. In fact these two methods are complementary in that light scattering probes, principally, fluctuations in the thermodynamic variables whereas Brownian motion samples the fluctuations in the fluid velocity field.

The growth of fluctuations in the thermodynamic variables has been utilized successfully in light scattering studies of second order phase transitions. The extension of these methods to the study of the enhancement of fluctuations in hydrodynamic regime transitions has been reviewed recently [17]. Unfortunately, because the correlation length is very large (of order

$d\varepsilon^{-1/2}$ , i.e. much longer than that for phase transitions), of the fluctuations, only the Fourier components with wave vectors quite close to the critical value are significantly enhanced. Since the critical wave vector is of order  $d^{-1}$  it is apparent, taking  $d = 1$  cm, that large fluctuations can be expected only for observations at scattering angles of  $10^{-3}$  to  $10^{-4}$  radians. Intensity measurements at such angles present a non-trivial technical problem and so far no experimental evidence for enhanced fluctuations near the convective instability have been produced [18].

Using Faxen's theorem the diffusion coefficient of Brownian particles can be related to the fluctuations in the fluid velocity field [19]. Due to the enhancement of the fluid velocity fluctuations near the hydrodynamic instability point the diffusion coefficient consists of a critical contribution that within the framework of linear fluctuation theory increases as  $\varepsilon^{-3/2}$  as well as the regular contribution given by the Stokes-Einstein expression. We write the diffusion coefficient of the Brownian particles as

$$D = D^{\text{reg}} + A\varepsilon^{-3/2}$$

where the factor  $A$  can be calculated from the fluid velocity fluctuation correlation function and is proportional to  $C^{(w)}/\alpha^2$  where  $C^{(w)}$  and  $\alpha$  are defined by eqs. (17) and (19) for the binary mixture and by eqs. (20) and (21) for the one component fluid. It follows that this ratio  $A$  is in fact formally the same for the one and two component Rayleigh-Bénard instability. As pointed out in earlier work [19] the enhancement of  $D$  is significant. For example for the case where  $d = 1$  cm and the radius of the Brownian particle is  $10^3 \text{ \AA}$  then for  $\varepsilon = 10^{-3}$ , the critical part of  $D$  is of the order of 10 % of  $D^{\text{reg}}$  and for  $\varepsilon = 10^{-4}$  the critical part of  $D$  is of the order of 10 times  $D^{\text{reg}}$ . Thus the study of Brownian motion could provide a real opportunity to probe the pretransitional region.

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