

Non-Oberbeck-Boussinesq effects and barodiffusion in binary mixtures with small thermodiffusion ratio

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For a binary-fluid layer heated from below, we evaluate the effects of the temperature and concentration dependence of the thermodiffusion ratio k_T as well as the influence of barodiffusion on the conductive state and its stability.

Fluid layers of binary mixtures¹⁻³ heated from below have attracted in the last few years ever-growing experimental⁴⁻¹⁰ and theoretical¹¹⁻¹³ research activity aimed at understanding the rich and interesting bifurcation phenomena arising out of the basic conductive state. Some of these take place near the so-called codimension-two (CT) point¹¹ in the plane of control parameters spanned by the Rayleigh number and, e.g., the separation ratio ψ_0 .¹¹ There an oscillatory and a stationary convective instability compete. Stability analyses¹¹⁻¹⁴ using the Oberbeck-Boussinesq^{3,14} (OB) approximation show that the ψ_0 coordinate of the CT point, being proportional to the square of the Lewis number, is very small for the mixtures used in experiments.⁴⁻¹⁰ Since ψ_0 , on the other hand, is basically determined by the thermodiffusion ratio k_T , the latter is vanishingly small and with it, also, the concentration gradient across the layer evaluated in the OB approximation without barodiffusion.

For such a situation, we investigate the non-Oberbeck-Boussinesq (NOB) effects of incorporating the variation of k_T with temperature and concentration across the layer, and of the barodiffusion contribution to the concentration current on (i) the conductive concentration profile and (ii) the stability behavior of the conductive state.

The field equations. The hydrodynamic field equations describing binary mixtures that are incompressible except for buoyancy effects are^{1-3,14}

$$\rho_0(\partial_t + \mathbf{u} \cdot \nabla) \mathbf{u} = -\nabla p + \rho \mathbf{g} + \rho_0 \nu \nabla^2 \mathbf{u} , \quad (1a)$$

$$\rho_0(\partial_t + \mathbf{u} \cdot \nabla) c = -\nabla \cdot \mathbf{J}_c , \quad (1b)$$

$$\rho_0 c_p (\partial_t + \mathbf{u} \cdot \nabla) T = \varepsilon + [\mu - T(\partial \mu / \partial T)_{c,p}] \nabla \cdot \mathbf{J}_c - \nabla \cdot \mathbf{J}_e , \quad (1c)$$

$$\nabla \cdot \mathbf{u} = 0 . \quad (1d)$$

Here \mathbf{u} , p , c , T are the fields of velocity, pressure, concentration, and temperature, respectively. Furthermore, \mathbf{g} is the gravitational acceleration, ν the kinematic viscosity, c_p the specific heat at constant p and c , and μ the chemical potential.¹ The density of energy dissipation ε will be ignored in the following. For small variations of T , p , c around a reference state, identified in the following by an index 0, the equation of state¹⁻³

$$\rho = \rho_0 [1 - \alpha_0 (T - T_0) - \beta_0 (c - c_0)] , \quad (2a)$$

for the mass-density field ρ may be used in the buoyancy

term in (1a). The expansion coefficients

$$\begin{aligned} \alpha_0 &= - (1/\rho_0) (\partial \rho / \partial T)_{c,p}^0 , \\ \beta_0 &= - (1/\rho_0) (\partial \rho / \partial c)_{T,p}^0 , \end{aligned} \quad (2b)$$

are evaluated in the reference state, e.g., at the upper plate of an experimental convection cell. We shall ignore the density variation induced by the compressibility $\chi_0 = (1/\rho_0) (\partial \rho / \partial p)_{c,T}^0$.

The diffusive currents of concentration and energy are given by¹⁻³

$$\mathbf{J}_c = -\rho_0 D [\nabla c + k_T (\nabla T / T) + k_p (\nabla p / p)] , \quad (3a)$$

$$\begin{aligned} \mathbf{J}_e &= -\rho_0 c_p \chi \nabla T + [k_T (\partial \mu / \partial c)_{T,p} \\ &\quad + \mu - T (\partial \mu / \partial T)_{c,p}] \mathbf{J}_c , \end{aligned} \quad (3b)$$

where D is the diffusion coefficient, k_T the thermodiffusion ratio, k_p the barodiffusion ratio, and χ the thermodiffusivity.

If the Dufour effect, i.e., the coupling of the temperature field to the concentration current is small, one may ignore in (1c) all contributions into which \mathbf{J}_c enters. Here we shall do that.

Modified OB approximation. So far all quantities, except those for the reference state, are still fields depending on (\mathbf{r}, t) , e.g., via a (T, c, p) dependence. In the standard OB approximation^{3,14} one ignores the (\mathbf{r}, t) dependence of ν , D , χ , k_p , k_T , c_p , μ and takes the values in the reference state. Furthermore, T and p in the currents (3) are replaced by T_0 and p_0 , since the relative deviations $\Delta T / T_0$ and $\Delta p / p_0$ are small in the standard convection experiments.⁴⁻¹⁰ In addition, the barodiffusion contribution is commonly ignored^{3,11-14} by setting k_p equal to zero.

However, to describe mixtures with very small k_T^0 , e.g., onset of convection near the CT point, where k_T^0 is almost zero it might be necessary to incorporate in the concentration current \mathbf{J}_c (i) the variation of k_T across the fluid layer and (ii) the barodiffusion contribution. To that end we (i) expand k_T around the reference state

$$k_T = k_T^0 + (\partial k_T / \partial T)_{c,p}^0 (T - T_0) + (\partial k_T / \partial c)_{T,p}^0 (c - c_0) , \quad (4)$$

ignoring a variation of k_T with pressure, and (ii) we use¹

$$k_p^0 = p \beta_0 / \rho_0 (\partial \mu / \partial c)_{T,p}^0 . \quad (5)$$

For definitiveness we shall consider, henceforth, a fluid layer of height d between impervious perfectly heat conducting horizontal plates. They impose the temperature T_0 at the top $z=d$, and $T_0+\Delta T$ at the bottom $z=0$, such that

$$R = (\alpha_0 g d^3 / \chi_0 \nu_0) \Delta T, \quad (6)$$

is the associated Rayleigh number. For R close to the threshold for onset of convection the relative variation of the other thermodynamic and transport quantities across the fluid layer is small in a typical experimental setup⁴⁻¹⁰ and will, thus, be ignored here.

If one scales length by d , time by d^2/χ_0 , temperature by $\chi_0 \nu_0 / \alpha_0 g d^3$, concentration by $\chi_0 \nu_0 / \beta_0 g d^3$, and p/ρ_0 by χ_0^2 / d^2 the field equations (1) reduce with the above described approximations to

$$\begin{aligned} (\partial_t + \mathbf{u} \cdot \nabla) \mathbf{u} &= -\nabla(p + \hat{g}z) \\ &+ \mathbf{e}_z \sigma_0 (T - T_0 + c - c_0) + \sigma_0 \nabla^2 \mathbf{u}, \end{aligned} \quad (7a)$$

$$(\partial_t + \mathbf{u} \cdot \nabla) c = L_0 \nabla \cdot [\nabla c - \psi \nabla T + \Gamma_0 \nabla p / \hat{g}], \quad (7b)$$

$$(\partial_t + \mathbf{u} \cdot \nabla) T = \nabla^2 T. \quad (7c)$$

Here $\sigma_0 = \nu_0 / \chi_0$ is the Prandtl number, $L_0 = D_0 / \chi_0$ is the Lewis number, $\hat{g} = g d^3 / \chi_0^2$ is the dimensionless gravitational acceleration, and

$$\Gamma_0 = (g^2 d^4 \beta_0^2 / \nu_0 \chi_0) / (\partial \mu / \partial c)_{T,p}^0 \quad (8)$$

measures the barodiffusion ratio. Note that Γ_0 increases with the fourth power of the height of the fluid layer. Our estimate for the experimental setup⁵ for a ${}^3\text{He}$ - ${}^4\text{He}$ mixture¹⁵ is $\Gamma_0 \approx 0.2$ and for ethanol-water mixtures (Ref. 16) $\Gamma_0 \approx 0.05$. Let us stress that some of the numbers^{15,16} estimated in this paper are based, in the absence of more complete experimental data, on somewhat daring guesses which, however, do not influence the theoretical results presented here.

NOB effects enter via the separation ratio

$$\psi = -(\beta_0 / \alpha_0 T_0) k_T, \quad (9a)$$

which still depends, via k_T Eq. (4), on the local temperature and concentration

$$\psi = \psi_0 + \varphi_T^0 (T - T_0) + \varphi_c^0 (c - c_0) \quad (9b)$$

with expansion coefficients

$$\varphi_T^0 = -(\nu_0 \chi_0 \beta_0 / g d^3 \alpha_0^2 T_0) (\partial k_T / \partial T)_{p,c}^0, \quad (9c)$$

$$\varphi_c^0 = -(\nu_0 \chi_0 / g d^3 \alpha_0 T_0) (\partial k_T / \partial c)_{p,T}^0. \quad (9d)$$

In many theoretical^{3,11-13} and experimental⁴⁻¹⁰ works the separation ratio ψ_0 is taken as the second control parameter besides R . For the ${}^3\text{He}$ - ${}^4\text{He}$ experiments⁵ we estimate¹⁵ $\varphi_T^0 \approx 2 \times 10^{-6}$ and $\varphi_c^0 \approx -8 \times 10^{-8}$. For the experiments^{7,8} using ethanol-water mixtures we estimate (Ref. 16) $\varphi_c^0 \approx -1.7 \times 10^{-6}$ and we guess¹⁶ very roughly $|\varphi_T^0| \approx 10^{-5}$. Note that for fixed Rayleigh number both NOB effects increase $\sim d^{-3}$ with decreasing height d of the fluid layer. The reason⁶ is that the variation $k_T - k_T^0$ of the thermodiffusion ratio [Eq. (4)] across the layer grows linearly with the temperature difference $T - T_0$,

which, for fixed Rayleigh numbers R , Eq. (6) increases $\sim d^{-3}$.

The conductive state. We first investigate the effects of NOB terms and of barodiffusion on the stationary conductive state $\mathbf{u} = \mathbf{0}$ and $\mathbf{J}_c = \mathbf{0}$. Note that the absence of a concentration current in the stationary conductive state between rigid plates implies that there is no Dufour effect. Then the temperature profile is linear

$$T_{\text{cond}}(z) - T_0 = R(1 - z). \quad (10)$$

Since the gravitational force \hat{g} is in general much larger than the bouyancy force $\sigma_0[R(1 - z) + c_{\text{cond}}(z) - c_0]$, one also finds that the pressure varies linearly across the layer

$$p_{\text{cond}}(z) - p_0 = \hat{g}(1 - z). \quad (11)$$

The concentration profile is determined by $\mathbf{J}_c = \mathbf{0}$, i.e., by the solution of

$$(\partial_z + R\varphi_c^0)[c_{\text{cond}}(z) - c_0] = -R\psi_0 + \Gamma_0 - R^2\varphi_T^0(1 - z), \quad (12)$$

where $c_0 = c_{\text{cond}}(z=1)$ is the concentration at the upper plate. Without NOB effects, $\varphi_c^0 = \varphi_T^0 = 0$, the conductive concentration profile would be linear with a gradient

$$s_0 = -R\psi_0 + \Gamma_0. \quad (13)$$

Hence, the barodiffusion contribution has to be included whenever Γ_0 becomes comparable in size with $R\psi_0$. Thus, near the CT point where R is about 1700 and $-\psi_0$ is about a few 10^{-4} , this contribution to the conductive concentration gradient should not be ignored in ${}^3\text{He}$ - ${}^4\text{He}$ mixtures.¹⁵

Both NOB terms φ_T^0 and φ_c^0 cause nonlinearities in the conductive concentration profile

$$\begin{aligned} c_{\text{cond}}(z) - c_0 &= -s_0(1 - z)a_1(z) \\ &+ \frac{1}{2} R^2 \varphi_T^0 (1 - z)^2 a_2(z), \end{aligned} \quad (14a)$$

$$a_1 = (e^\tau - 1)/\tau; \quad a_2 = 2(a_1 - 1)/\tau; \quad \tau = \varphi_c^0 R(1 - z). \quad (14b)$$

The functions $a_1(z)$ and $a_2(z)$ that reflect the NOB effect due to the concentration dependence of k_T across the layer approach 1 for small φ_c^0 . In recent convection experiments (Refs. 4-10) $|\varphi_c^0 R|$ seems to have been less than 10^{-2} in which case a_1 and a_2 may be effectively replaced by 1.

However, the NOB effects due to the temperature variation of k_T seem to be larger and will be noticeable in any case in Eq. (14) when $s_0 = -R\psi_0 + \Gamma_0$ becomes comparable with $R^2\varphi_T^0$. That happens in the vicinity of the CT point: our estimates at the convection threshold $R_c \sim 1700$ are $R_c \varphi_T^0 \approx +3.4 \times 10^{-3}$ for ${}^3\text{He}$ - ${}^4\text{He}$ mixtures¹⁵ and $R_c |\varphi_T^0| \approx 1.7 \times 10^{-2}$ for ethanol and water.¹⁶ In any case Eq. (14) is our result for the conductive concentration profile.

Stability of the conductive state. We finally discuss some of the changes in the stability behavior of the conductive state brought about by barodiffusion and NOB

effects. The linear field equations are

$$(\partial_t - \sigma_0 \nabla^2) \nabla^2 w = \sigma_0 (\partial_x^2 + \partial_y^2) (\theta + c) , \quad (15a)$$

$$\partial_t c + (-R \psi_{\text{cond}} + \Gamma_0) w = L_0 \nabla^2 (c - \psi_{\text{cond}} \theta) + h , \quad (15b)$$

$$\partial_t \theta - R w = \nabla^2 \theta . \quad (15c)$$

Here w is the vertical velocity field, θ and c are the deviations of the temperature and concentration field from the conductive state, and

$$\psi_{\text{cond}}(z) = \psi_0 + \varphi_T^0 R (1 - z) + \varphi_c^0 [c_{\text{cond}}(z) - c_0] \quad (15d)$$

denotes the vertical dependence of the separation ratio (9b) for the conductive profiles of temperature and concentration. The field h is given by

$$h = L_0 \varphi_c^0 [R \partial_z c + \partial_z \theta \partial_z c_{\text{cond}} + \theta \partial_z^2 c_{\text{cond}}] + L_0 \sigma_0 (\Gamma_0 / \hat{g}) \partial_z (\theta + c) . \quad (16)$$

To derive Eqs. (15) and (16) we used

$$\partial_z c_{\text{cond}} + R \psi_{\text{cond}} - \Gamma_0 = 0 \quad (17)$$

which is equivalent to Eq. (12).

In the following we shall discuss only the situation where $|R \varphi_c^0| \ll 1$ and ignore h altogether in Eq. (15b) given that $L_0 \sigma_0 \Gamma_0 / \hat{g}$ and $L_0 R \varphi_c^0$ are vanishingly small. The remaining linear problem (15)—already difficult with a constant ψ —is complicated further by the z variations of $\psi_{\text{cond}}(z)$ [Eq. (15d)] such that a proper solution requires a full numerical approach. However, it is clear from inspecting the magnitudes of the coefficients in Eq. (15b) that the gradient $\partial_z c_{\text{cond}}(z) = -R \psi_{\text{cond}}(z) + \Gamma_0$ of the conductive concentration profile, which couples the concentration field c in Eq. (15b) to the vertical velocity field w , is the dominant term to cause the changes. The coupling to the convective temperature field θ on the right-hand side of (15b) is much smaller, since the Lewis number L_0 is negligibly small compared to R . We have verified this explicitly for free slip, permeable horizontal boundaries and also with a truncated Galerkin approximation¹³ for free-slip, impermeable boundaries.

Here we only want to *estimate* the effects of NOB terms and of barodiffusion on the stability properties of the conductive state. Thus, in view of the fact that $\psi_{\text{cond}}(z)$ varies mildly across the fluid layer, we replace $\psi_{\text{cond}}(z)$ by its value at midheight

$$\psi_{\text{cond}}(z) \rightarrow \psi_{\text{cond}}(\frac{1}{2}) = \psi_0 + \frac{1}{2} \varphi_T^0 R , \quad (18)$$

ignoring again terms $\sim R \varphi_c^0$. Then the stability curves (dashed and solid lines in Fig. 1) in the $R - \psi_0$ plane are shifted in the vicinity of $\psi_0 = 0$ to positive ψ_0 by the amount Γ_0 / R_c by the barodiffusion term. The NOB effect due to the temperature variation of k_T , on the other hand, shifts the threshold curves by $-\frac{1}{2} \varphi_T^0 R_c$ along the ψ_0 axis, as indicated schematically in Fig. 1. For ³He-⁴He (ethanol and water) mixtures our estimates for the former shift are about 10^{-4} (3×10^{-5}) and about -1.7×10^{-3} [\pm (?) 9×10^{-3}]. We once more stress that the above estimates are based partly on guesses.

Measurements. The displacement of the stability curves along the ψ_0 axis causes the critical Rayleigh num-

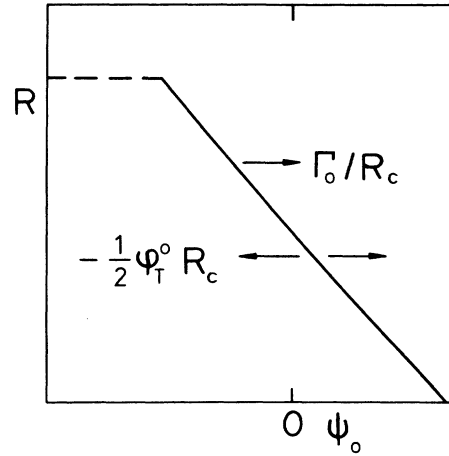


FIG. 1. Schematic stability diagram of the conductive state in the vicinity of the intersection of thresholds for onset of oscillatory (dashed line) and stationary (solid line) convection. Barodiffusion displaces the stability thresholds parallel to the ψ_0 axis by the amount Γ_0 / R_c . Temperature variation of k_T across the fluid causes a shift of $-0.5 \varphi_T^0 R_c$ along the ψ_0 axis.

ber, for onset of convection, to be shifted at a fixed ψ_0 by

$$\delta R_c \approx (\partial R_c / \partial \psi_0) [\frac{1}{2} \varphi_T^0 R_c - \Gamma_0 / R_c] , \quad (19a)$$

relative to the OB convective threshold. Similarly the associated critical wave number is shifted by

$$\delta k_c \approx (\partial k_c / \partial \psi_0) [\frac{1}{2} \varphi_T^0 R_c - \Gamma_0 / R_c] , \quad (19b)$$

relative to the OB result. These changes brought about by the above-discussed approximate replacement $\psi \rightarrow \psi_0 + \frac{1}{2} \varphi_T^0 R_c - \Gamma_0 / R_c$ are largest for the stationary convective instability. In that case R_c and k_c are both strongly varying functions of ψ_0 near $\psi_0 = 0$ so that the derivative prefactors in Eq. (19) are large. From a Galerkin model¹³ with free-slip, impermeable boundaries one estimates

$$\partial R_c / \partial \psi_0 = -R_c [24 / (\pi^2 L_0) + 1] ,$$

and

$$\partial k_c / \partial \psi_0 = -k_c [12 / (\pi^2 L_0)] ,$$

so that the associated relative variations are quite large of order -10^2 in the commonly used⁴⁻¹⁰ fluids.

The results (19) imply predictions for experiments that compare onset properties of convection in fluid layers of different heights λd and d , respectively, with T_0, c_0 in both cases being the same: For small ψ_0 the convective threshold and the critical wave number of the former should be shifted relative to those of the latter by

$$\Delta R_c \approx \frac{\partial R_c}{\partial \psi_0} \left[(\lambda^{-3} - 1) \frac{1}{2} \varphi_T^0 R_c - (\lambda^4 - 1) \frac{\Gamma_0}{R_c} \right] \quad (20a)$$

$$\Delta k_c \approx \frac{\partial k_c}{\partial \psi_0} \left[(\lambda^{-3} - 1) \frac{1}{2} \varphi_T^0 R_c - (\lambda^4 - 1) \frac{\Gamma_0}{R_c} \right] . \quad (20b)$$

Here $R_c, k_c, \varphi_T^0, \Gamma_0$ applies to the layer of thickness d . For

small d and $\lambda < 1$ (large d and $\lambda > 1$) the NOB (barodiffusion) effect represented by the first (second) term in the large parenthesis dominates the shifts.

The predictions (20) for the variation of the convective threshold and the critical wave number with the height of the fluid layer are, besides the changes in the conductive concentration profile (14), the simplest manifestations of NOB effects and barodiffusion close to $\psi_0 = 0$. Other

questions, e.g., the precise modification of the stability behavior near the CT point of the standard OB approximation or the influence on stationary and oscillatory convective states are still open questions.

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- ¹⁴G. Z. Gershuni and E. M. Zhukhovitskii, *Convective Stability of Incompressible Fluids* (Keter, Jerusalem, 1976).
- ¹⁵Our estimates for ³He-⁴He mixtures are based on an extrapolation of data of Ref. 4 to a molar concentration $x = 0.03$ ($c_0 = 0.023$) and temperature $T_0 \approx 2.225$ K where k_T^0 seems to vanish. We used $v_0 \approx 2 \times 10^{-4}$ cm²/sec, $\alpha_0 \approx 3 \times 10^{-4}$ cm²/sec, $\beta_0 \approx 0.7$, $\partial\mu/\partial c \approx 3.5 \times 10^9$ cm²/sec² (2.5×10^9 cm²/sec² if ³He and ⁴He were ideal gases), $\partial k_T/\partial T \approx -0.03$ /K (which is comparable to an estimate in Ref. 6), $\partial k_T/\partial c \approx 0.05$, and $d = 0.1$ cm.
- ¹⁶For ethanol water mixtures k_T^0 vanishes (cf. Ref. 8) at $T_0 \approx 283$ K, $c_0 \approx 0.3$. We used $v_0 \approx 10^{-2}$ cm²/sec, $\alpha_0 \approx 10^{-3}$ cm²/sec, $\beta_0 \approx 3 \times 10^{-4}$ /K, $\partial\mu/\partial c \approx 3.2 \times 10^9$ cm²/sec² (if ethanol and water were ideal gases), $|\partial k_T/\partial T| \approx 0.03$ /K (lacking data we use the He value), $\partial k_T/\partial c \approx 1.8$, and $d = 0.5$ cm. If one would multiply $\partial k_T/\partial c$ with the He quotient of $(\partial k_T/\partial T)/(\partial k_T/\partial c)$ one would obtain an estimate for $|\partial k_T/\partial T| \approx 1.1$ /K which, being so big, would entail an enormous NOB effect. Clearly, experimental data are called for.