

## Separation ratio, Dufour number, and advection-diffusion equations of Lorentz gas mixtures

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Based on well-known results from the kinetic theory of gases, we give approximate formulas relating the separation ratio of gas mixtures to the diffusion coefficient, the concentration, and the temperature for the case of a dilute mixture of a light, monoatomic component in a much heavier one (Lorentz gas mixture). Beyond that, we calculate the Dufour number for this case and give an explicit relation which shows that the separation ratio and the Dufour number are inversely proportional. The knowledge of the separation ratio and the Dufour number is important for the study of convection in gas mixtures. We apply the results by providing a modified set of advection-diffusion equations appropriate to Lorentz gas mixtures.

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### I. INTRODUCTION

Most of the studies of convection in binary fluid mixtures have focused on liquid mixtures. During the last decade, a considerably deep understanding of their properties has been achieved (for a recent overview, see Ref. [1]). Convection in gas mixtures [1], however, is less well understood. In gas mixtures, the time scales for thermal and mass diffusion are of the same order and are not distinct by a factor of about 100 as in liquid mixtures. Recently, theoretical work [2–4] on convection in gas mixtures has shown that their instabilities to convection can be quite different from that of liquid mixtures, provided that the Dufour effect is large and the separation ratio (which is related to the thermodiffusion effect) is not too close to zero [2,3]. There are many open questions, if one is interested in experimental investigations in this system. To perform experiments in the Rayleigh-Bénard setup, one is confronted with the problem that one needs information about several thermodynamic and transport properties of the binary mixture. In particular, the separation ratio  $\psi$  and the Dufour number  $Q$  are important. Beside the Rayleigh number, they are two further control parameters which appear in the nondimensional fluid dynamic equations. Knowledge of them is important for reaching ranges of control parameters where one can see the new interesting features [2–4]. For an arbitrary gas mixture, it seems to be impossible to estimate theoretically the separation ratio based on easier measurable quantities. In this Brief Report, we provide several approximate relations for the separation ratio and the Dufour number for a special class of gas mixtures, the *diffusion of a dilute mixture of a light, monoatomic component in a heavy component*. As an application, we also provide the set of advection-diffusion equations which serve as an appropriate starting point to study convection in Lorentz gases. We take advantage of well-known analytic results from the kinetic theory of gases [6,7] and simple ideal gas mixture approximations to gain more insight into the physics behind the separation ratio and the Dufour number.

### II. SEPARATION RATIO FOR LORENTZ GAS MIXTURES

The separation ratio [1] is given by

$$\psi = -\frac{\beta}{\alpha} \frac{k_T}{T}. \quad (1)$$

Here,  $\beta = -(1/C)(\partial\rho/\partial C)_{T,p}$  and  $\alpha = -(1/T)(\partial\rho/\partial T)_{C,p}$  are the solutal and thermal expansion coefficients;  $\rho$  is the total mass density, i.e., the sum of the mass densities of the two components,  $\rho = \rho_1 + \rho_2$ . The concentration  $C$  is defined by the ratio of the mass density  $\rho_1$  of the lighter component and the total mass density  $\rho$ ,  $C = \rho_1/\rho$ .  $T$  denotes the temperature,  $p$  the pressure, and  $k_T$  the thermodiffusion coefficient of the mixture.  $k_T$  [5], a transport coefficient, is basically the coupling coefficient of the heat flux in the equation for the mass flux of one component (“Soret effect”) and thus a quantity being determined as a combination of Onsager coefficients. It cannot be calculated easily, and exact theories based on Boltzmann’s equation [7] are not very practical, since there are several microscopic, usually unknown parameters involved.

First, one can approximate  $\alpha$  by its ideal gas value  $T^{-1}$ , which implies  $\psi = -\beta k_T$ , provided there are normal temperature and pressure conditions. Second, we recall that the solutal expansion coefficient  $\beta$  is positive as a result of thermodynamic considerations [6]. Using an ideal gas mixture approximation (see, e.g., Refs. [2,3]), one can calculate  $\beta$  explicitly, yielding

$$\beta = \frac{1 - m_*}{(1 - C)m_* + C}, \quad (2)$$

where  $m_* = m_1/m_2$  is the ratio of particle masses  $m_1$  and  $m_2$  of the two components. From Eq. (2) one can see that large  $\beta$  can be reached for small particle mass ratios  $m_* \ll 1$  and dilute mixtures  $C \ll 1$ . This is intuitively clear, since  $\beta$  basically measures the density changes due to the replacing of a particle of one component by one of the other. This is large when the differences of the parti-

cle masses are large. The kinetic theory of gases, cf. Ref. [7], gives in the limit of a mixture of a *dilute, light, monoatomic* component in a *much heavier* component, which is called a Lorentz gas mixture, the following relations [7] for the diffusion coefficient  $D$  and the thermodiffusion ratio  $k_T$ :

$$D = \frac{k_B T}{3\rho m_* (1-C)^2} \langle v/\sigma_t \rangle, \quad (3)$$

$$k_T = CT \partial_T \ln \frac{\langle v/\sigma_t \rangle}{T}. \quad (4)$$

Here,  $\sigma_t$  denotes the collision cross section,  $v$  the velocity of the lighter particles, and the brackets denote averaging over a Maxwellian velocity distribution [7].

In this special case, one considers the heavy particles as almost fixed in space, and only collisions of the lighter with the heavier particles are taken into account. Let us note the range of validity of these formulas: (i) The particle mass of the dilute component  $m_1$  has to be much smaller than  $m_2$ ; (ii) the mixture has to be dilute in the sense that  $m_*(1-C)$  is large in comparison to  $C$ ; and (iii) gradients of temperature and concentration act only in one space dimension.

Eliminating  $\langle v/\sigma_t \rangle$  from Eqs. (3) and (4) and using Eq. (2) yield

$$\psi = -\frac{1-m_*}{m_*(1-C)} C [T \partial_T \ln D(T) - 2]. \quad (5)$$

This simple relation basically connects the separation ratio  $\psi$  with the diffusion coefficient  $D$ , which is experimentally easier to measure.

Several conclusions can be drawn from Eq. (5). (i) To calculate  $\psi$ , it is not necessary to know the value of the diffusion coefficient exactly; the logarithmic variation of the diffusion coefficient with temperature is sufficient. (ii) The separation ratio of a gas mixture is zero, if  $dD/D = 2dT/T$  or, equivalently, if the diffusion coefficient  $D$  has a quadratic dependence on the temperature,  $D(T) = \text{const} \times T^2$ . Thus, mixtures having temperature dependence with an exponent close to 2 are not good candidates for reaching larger separation ratios. (iii) Since  $m_* \ll 1$  and  $C$  is positive,  $\psi$  is positive (negative) if the variation of  $D(T)$  with  $T$  at temperature  $T$  is weaker (stronger) than quadratic. (iv) In the limit of vanishing concentration  $C \rightarrow 0$  the separation ratio  $\psi$  approaches zero linearly, since neither  $\beta$  nor the diffusion coefficient  $D$  behave anomalously in this limit.

Also, the diffusion coefficient  $D$  in gases is not a quantity which can be easily calculated. However, there is the empirical, power-law relationship [8]  $D = D(T) = D_0(T/T_0)^n$ , which is valid for a wide range of gas mixtures under normal pressure and temperature conditions. Here,  $T_0$  is a reference temperature and the exponent  $n$  can be determined experimentally and is tabulated for some mixtures [8]. Unfortunately, only few are known even of this quantity. The few, tabulated values [8] of  $n$  range from  $\frac{1}{4}$  to 2, suggesting that only positive  $\psi$  might be realistic, albeit that this does not exclude  $n > 2$  at all. Using the power-law behavior, one obtains

$$\psi = \frac{1-m_*}{m_*(1-C)} (2-n)C \simeq \frac{1-m_*}{m_*} (2-n)C, \quad (6)$$

a linear dependence of  $\psi$  on the concentration  $C$ . Since  $C/m_*$  has to be small in Lorentz gas mixtures, one cannot expect to reach large moduli of  $\psi$  in this limit.

### III. THE DUFOUR NUMBER OF A LORENTZ GAS MIXTURE

The Dufour number, a purely thermodynamic quantity, is part of the second cross-coupling coefficient (coupling of the mass flux of the lighter component to the heat flux) which determines the magnitude of the Dufour effect [5]. It is given by [2]

$$Q = \frac{T\alpha^2}{c_p \beta^2} \left[ \frac{\partial \mu}{\partial C} \right]_{T,p}. \quad (7)$$

Using the ideal gas result for  $Q$  from Ref. [3], approximating the specific heat  $c_p$  of the mixture by a linear interpolation of the specific heat of the single components  $c_{p,i}$ ,  $c_p(C) = c_{p,2} + (c_{p,1} - c_{p,2})C$ , and using the same approximations we made before, we obtain

$$Q = \frac{k_B}{m_2 c_p(C)} \frac{m_*}{(1-m_*)} \frac{1}{C} \simeq \frac{k_B}{m_2 c_{p,2}} \frac{m_*}{(1-m_*)} \frac{1}{C}. \quad (8)$$

Thus,  $Q$  diverges proportionally to  $1/C$  as  $C \rightarrow 0$  and can reach arbitrarily large values.

In the case of Lorentz gas mixture, the separation ratio  $\psi \sim C$  and the Dufour number  $Q \sim C^{-1}$  are *not* independently variable quantities in an experiment. They are connected by

$$Q\psi = \frac{k_B}{m_2 m_* c_p} [T \partial_T \ln D(T) - 2] \simeq \frac{k_B}{m_2 m_* c_{p,2}} (2-n). \quad (9)$$

Thus, the product  $Q\psi$  does not depend on the concentration and the Dufour number  $Q$  is inversely proportional to the separation ratio  $\psi$  in a Lorentz gas mixture. This also supports earlier speculations [4] about their relationship, albeit in [4], where a  $\text{CO}_2/\text{H}_2$  mixture had been discussed.

### IV. ADVECTION-DIFFUSION EQUATIONS FOR LORENTZ GAS MIXTURES

Let us now turn to the implications of Eqs. (6), (8), and (9) for convecting binary mixtures. The most common setup for convection experiments is the Rayleigh-Bénard experiment, a horizontal layer of a binary fluid subject to a constant temperature difference  $\Delta T$  between impermeable horizontal boundaries at  $z=0$  and  $d$ . Initially, if  $\Delta T=0$ , the concentration is constant everywhere in the layer, as given by  $C(x,z) = \bar{C}$ . When  $\Delta T$  is increased, only the mean concentration  $\int dx \int_0^d dz C(z)$  is equal to  $\bar{C}$  since the boundaries are impermeable. It appears quite natural to consider the mean concentration as a second control parameter (instead of the separation ratio  $\psi$ ). Using Eqs. (6) and (8), we can eliminate  $\psi$  and  $Q$  in favor of

the concentration  $C$  in the standard governing equations for gas mixtures [2-4,9]. It is important, however, that one take into account the full spatiotemporal dependence of  $C$  in Eqs. (6) and (8) since the mean concentration is small and therefore relative variations can be quite large (similar to calculations in Ref. [10]). Finally, one can perform an Overbeck-Boussinesq approximation [2-4,9], particularly by considering all thermodynamic and hydrodynamic coefficients in the advection-diffusion equations as being constant. The result is the following set of advection-diffusion equations for the velocity field  $\mathbf{u}$ , the concentration field  $C$ , and temperature field  $T$ , appropriate as a starting point to discuss Lorentz gas mixtures:

$$\begin{aligned} (\partial_t + \mathbf{u} \cdot \nabla) \mathbf{u} &= -\nabla(p + \hat{g}z) \\ &+ \mathbf{e}_z \sigma [T - T(z=1) + C - C(z=1)] \\ &+ \sigma \nabla^2 \mathbf{u}, \end{aligned} \quad (10a)$$

$$(\partial_t + \mathbf{u} \cdot \nabla) T = -\nabla \cdot \mathbf{J}_e + abC^{-1} \nabla \cdot (C \mathbf{J}_c), \quad (10b)$$

$$(\partial_t + \mathbf{u} \cdot \nabla) C = -\nabla \cdot \mathbf{J}_c, \quad (10c)$$

$$\nabla \cdot \mathbf{u} = 0. \quad (10d)$$

The diffusive heat and concentration fluxes  $\mathbf{J}_e$  and  $\mathbf{J}_c$  are given by

$$\mathbf{J}_e = -\nabla T, \quad \mathbf{J}_c = -L(\nabla C - aC\nabla T), \quad (10e)$$

and the dimensionless coefficients  $a$  and  $b$  are given by

$$a = \frac{\kappa\nu(1-m_*)}{\beta g d^3 m_*} (2-n), \quad b = \frac{\kappa\nu k_B m_*}{\beta g d^3 m_2 c_{p,2} (1-m_*)}. \quad (10f)$$

Here,  $\kappa$  is the thermal diffusivity,  $\nu$  the kinematic viscosity,  $\sigma = \nu/\kappa$  the Prandtl number,  $L = D/\kappa$  the Lewis number,  $g$  the gravity acceleration, and  $\hat{g} = g d^3/\kappa^2$ . In writing Eqs. (10a)-(10f) we scaled lengths by layer thickness  $d$ , times by  $d^2/\kappa$ , temperatures by  $\kappa\nu/\alpha g d^3$ , concentrations by  $\kappa\nu/\beta g d^3$ , and the reduced pressure  $p$  by  $\kappa^2/d^2$ . Equations (10) must be solved with appropriate boundary conditions, in particular no vertical mass flux at  $z=0$  and  $1$ , constant mean concentration  $\bar{C}$ , and fixed temperature  $T(z=1) = T_0$  and  $T(z=0) = T_0 + R$ . Here  $R$  is the Rayleigh number (the nondimensionalized temperature difference between the boundaries).

Two remarks are in order. (i) For a chosen mixture, the coefficients entering in  $a$  and  $b$  can be considered as constants, since  $\beta \approx 1/m_*$ . The only two experimentally variable parameters are the Rayleigh number and mean concentration. (ii) A reasonable further approximation is to neglect all terms in Eqs. (10), which are quadratic in gradients of concentration and/or temperature. Then, the cross-coupling coefficient belonging to  $\nabla^2 C$  in Eq. (10b) is a constant.

## V. CONDUCTIVE STATE

The conductive state,  $\mathbf{u}=0$ ,  $T$  and  $C$  independent of time, can be easily found by solving the equation for the conductive mass flux  $\partial_z C - \psi \partial_z T = \partial_z C - aCR = 0$  with

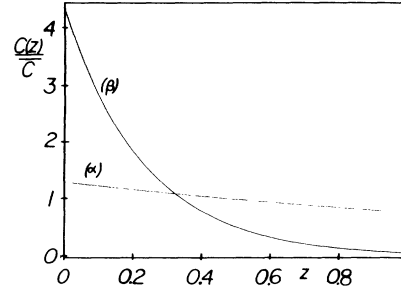


FIG. 1. Vertical concentration stratification  $C(z)/\bar{C}$ , Eq. (11), of a Lorentz gas mixture in the conductive state for two different values of the layer thickness,  $(\alpha) d=0.2$  cm,  $(\beta) d=0.1$  cm. The Rayleigh number is  $R=1708$ , the value of the convective instability of a pure fluid.

the constraint that  $\bar{C} = \int_0^1 C(z) dz$  is constant. The result is

$$C(z) = \bar{C} \frac{a \operatorname{Re}^{-aRz}}{1 - e^{-aR}}. \quad (11)$$

Depending on the magnitude of  $a$ , the conductive concentration  $C(z)$  can vary in a strongly nonlinear way. Only if  $aR$  approaches zero will  $C(z)$  be linear. Note that the parameter  $a$ , given in Eq. (10f), scales as  $d^{-3}$  and thus can be varied over several decades by varying the layer height. For gas mixtures,  $\kappa=0.1$  cm<sup>2</sup>/sec and  $\nu=0.1$  cm<sup>2</sup>/sec are quite typical [2,3]. Using these values, Eq. (2),  $n=1.75$ , one obtains  $a \approx 2.5 \times 10^{-6} d^{-3}$  cm<sup>3</sup>. In Fig. 1 we show for this set of parameters,  $R=1708$ , and two different layer heights,  $d=0.2$  and  $0.1$  cm, the vertical conductive concentration stratification  $C(z)/\bar{C}$ . Already, for  $d=0.1$  cm, one can see a boundary layer of higher concentration close to the lower boundary. This effect becomes even more pronounced for a layer thickness  $d=0.05$  cm, as used in recent convection experiments in one-component gases [12]. Equation (11) can also serve as a check of the relations provided in this paper, if the conductive concentration distribution is measured experimentally, as was done by Kolodner, Williams, and Moe [11] for liquid mixtures.

## VI. SUMMARY

We have given several simple, approximate relations for the separation ratio  $\psi$ , which can serve as a guide to estimate  $\psi$  in a Lorentz gas mixture. We have also given a relation for the Dufour number  $Q$  of a Lorentz gas mixture and shown that the product  $Q\psi$  does not depend on the concentration if  $C \ll 1$ . So far, the relations we provide are based on a linear diffusion process and, strictly speaking, are only applicable to conductive problems. In the case of convection, one should expect some deviations since the concentration and temperature gradients are not unidirectional. Nevertheless, Eqs. (10), provided in this paper, can be considered as a starting point to discuss convection in gas mixtures using only the Rayleigh number and the mean concentration as control parameter.

- [1] M. C. Cross and P. C. Hohenberg, *Rev. Mod. Phys.* **65**, 851 (1993).
- [2] S. J. Linz, *Phys. Rev. A* **40**, 7175 (1989); **45**, 1262 (1992).
- [3] W. Hort, S. J. Linz, and M. Lücke, *Phys. Rev. A* **45**, 3737 (1992).
- [4] S. J. Linz, in *Pattern Formation in Complex Dissipative Systems*, edited by S. Kai (World Scientific, Singapore, 1992), p. 320.
- [5] L. D. Landau and E. M. Lifschitz, *Fluid Dynamics* (Pergamon, New York, 1959).
- [6] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1992).
- [7] E. M. Lifschitz and L. P. Pitajewski, *Physical Kinetics* (Pergamon, New York, 1981), Chap. I.
- [8] *American Institute of Physics Handbook*, edited by D. E. Gray (McGraw-Hill, New York, 1963), Sec. 2w.
- [9] R. P. Behringer, *Rev. Mod. Phys.* **57**, 657 (1984).
- [10] S. J. Linz and M. Lücke, *Phys. Rev. A* **36**, 3505 (1987).
- [11] P. Kolodner, H. Williams, and C. Moe, *J. Chem. Phys.* **88**, 6512 (1988).
- [12] E. Bodenschatz, J. R. de Bruyn, G. Ahlers, and D. S. Cannell, *Phys. Rev. Lett.* **67**, 3078 (1991).