Thermal Diffusion in a Sinusoidal Temperature Field

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Separation of liquid mixtures in a thermal gradient, known as the Ludwig-Soret effect or thermal diffusion, is governed by a nonlinear, partial differential equation. It is shown here that the nonlinear differential equation for a binary mixture can be reduced to a Hamiltonian system of equations and that a solution can be obtained for the linear problem. The calculation gives a closed form expression for the space and time dependence of the concentration profile of the mixture, valid at short times.

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The separation of liquid mixtures driven by a thermal gradient was discovered by Ludwig [1] in 1856, and was first treated theoretically by Soret [2]. Reviews of the theory of thermal diffusion, as described by nonequilibrium thermodynamics, can be found in Refs. [3,4]; calculations of the magnitude of the effect in gases are reviewed in Refs. [5,6]. Recently, a new technique based on the use of crossed laser beams to produce thermal gradients without the associated problem of convection has been introduced [7–10]. The method relies on interference in the electric fields of two phase coherent light beams to form an optical grating in a weakly absorbing liquid mixture, resulting in a sinusoidal temperature field [11]. The spatial distribution of the components of the mixture resulting from the Ludwig-Soret effect is then probed by a light beam directed at the Bragg angle to the optical grating. In this Letter, we discuss solutions of the partial differential equation that governs thermal diffusion in a one-dimensional geometry with an externally imposed sinusoidal temperature field corresponding to the grating experiment. An exact solution to the linearized differential equation without diffusion for the concentration profiles of a binary mixture is obtained.

Thermal diffusion in a binary mixture is governed by the coupled differential equations [4]

$$\rho c_P \frac{\partial T}{\partial t} = \nabla \cdot (\lambda \nabla T + \kappa \nabla c_1), \tag{1}$$

$$\frac{\partial c_1}{\partial t} = \nabla \cdot (c_1 c_2 D' \nabla T + D \nabla c_1), \tag{2}$$

where t is the time, ρ is the solution density, c_P is the specific heat capacity, λ is the thermal conductivity, T is the temperature above ambient, κ is a constant, D' is the thermal diffusion coefficient, D is the mass diffusion coefficient, and c_1 and c_2 are density fractions of the species that make up the solution or suspension. Since the total mass of the solution is the sum of the masses of the two components of the mixture, it follows that the densities satisfy $\rho_1 + \rho_2 = \rho$, where ρ_1 and ρ_1 are the densities of the the two components, and that the density fractions c_1 and c_2 add to unity, $c_1 + c_2 = 1$. The first term on the right-hand side of Eq. (1) describes the Fourier law for heat conduction; the second describes the production of a temperature change as a result of imposition of a concentration gradient, known as the Dufour effect. In Eq. (2) the first term on the right-hand side describes the Ludwig-Soret effect while the second describes mass diffusion. If a steady temperature of the form $T = T_0[1 + \sin(Kx)]$, where T_0 is a peak temperature, K is a wave number determined by the optical fringe spacing in the grating, and x is the coordinate, is maintained in the cell and the Dufour effect is taken as negligible [4], then Eq. (2) reduces to

$$\frac{\partial c(z,t)}{\partial \tau} = \alpha \frac{\partial}{\partial z}\{c(z,t)[1 - c(z,t)]\}\cos z + \frac{\partial^2 c(z,t)}{\partial z^2}, \tag{3}$$

where c_2 has been written in terms of c_1, and the subscript 1 is dropped from the density fraction c_1, where α, known as the thermal diffusion factor, is given by $\alpha = D'T_0/D$, and the dimensionless quantities τ and z given by $\tau = K^2 Dt$ and $z = Kx$ have been used. If the last term in Eq. (3) describing diffusion is ignored, then the differential equation of motion for $c(z,t)$ can be written

$$\frac{\partial c}{\partial \tau} = -\frac{df}{dz}, \tag{4}$$

where a "flux" $f(c, z)$ is defined [12] as

$$f(c, z) = -\alpha c(1 - c)\cos z. \tag{5}$$

Equation (4) is of the form of a conservation equation that expresses the buildup of c as a consequence of a gradient of a flux in space. Since $c(\Lambda, \tau) = c(0, \tau)$ for a periodic temperature field, where $\Lambda = 2\pi/K$, it follows from Eq. (4) that the integral of the density fraction over one optical fringe is independent of time and, hence, that

$$\int_0^{\Lambda} c(z, t)\, dz = c_0 \Lambda \tag{6}$$

for any time, where at $t = 0$, c_0 is the density fraction, assumed here to be a constant throughout the cell.

Now Eq. (4) written in terms of f becomes

$$\frac{\partial c}{\partial \tau} + \frac{\partial f}{\partial c}\frac{\partial c}{\partial z} + \frac{\partial f}{\partial z} = 0, \tag{7}$$

the solution to which can be found on the characteristic curve $z = \beta(\tau)$, where β is a solution to the equation

$$\frac{\partial \beta}{\partial \tau} = \frac{\partial f(c, z)}{\partial c}. \tag{8}$$

That $c(\beta(\tau), \tau)$ is a solution to Eq. (7) can be seen by differentiation of c with respect to τ, which gives

$$\begin{aligned}\frac{d}{d\tau} c(\beta(\tau), \tau) &= \frac{\partial c}{\partial \tau} + \frac{\partial c}{\partial \beta}\frac{\partial \beta}{\partial \tau} = \frac{\partial c}{\partial \tau} + \frac{\partial f}{\partial c}\frac{\partial c}{\partial \beta} \\ &= -\frac{\partial f(c, \beta(\tau))}{\partial z},\end{aligned} \tag{9}$$

provided the equations

$$\frac{\partial \beta}{\partial \tau} = \frac{\partial f(c, \beta)}{\partial c}, \tag{10}$$

$$\frac{\partial c}{\partial \tau} = -\frac{\partial f(c, \beta)}{\partial \beta}, \tag{11}$$

are satisfied. The solutions to Eqs. (10) and (11) are thus solutions to the one-dimensional Ludwig-Soret problem without diffusion, as given by Eq. (4). It is noteworthy that Eqs. (10) and (11) form a Hamiltonian system, analogous to the well-known canonical equations of Hamilton found in classical mechanics, with f taking on the role of the Hamiltonian function.

Many of the features of the solution to Eq. (3) can be seen by linearizing f, which gives the profile of the density fraction for short times or as long as c is small compared with unity. By replacing f with its linearization around the constant state f_l given by $f_l(c, x) = -\alpha c \cos z$, the canonical equations become

$$\frac{dz}{d\tau} = -\alpha \cos z = \frac{\partial f_l}{\partial c}, \tag{12}$$

$$\frac{dc}{d\tau} = -\alpha c \sin z = -\frac{\partial f_l}{\partial z}. \tag{13}$$

Integration of Eq. (12) over the range 0 to τ gives

$$\frac{\cos z}{1 + \sin z} = e^{-\alpha\tau}\frac{\cos\zeta}{1 + \sin\zeta}, \tag{14}$$

which can be solved for $\sin z$ and written in a notation that expresses z in terms of τ and the integration constant ζ as

$$\sin[z(\tau; \zeta)] = \frac{\cosh(\alpha\tau)\sin\zeta - \sinh(\alpha\tau)}{\cosh(\alpha\tau) - \sinh(\alpha\tau)\sin\zeta}, \tag{15}$$

where ζ corresponds to the value of z at $\tau = 0$. A plot of the characteristic curves that represent the "natural coordinates" of the differential equation is shown in Fig. 1. Now on a single characteristic curve it is possible to arrive at $z(\tau, \zeta)$ by going directly from 0 to τ, or, to go indirectly, by first going a time σ to $z(\sigma, \zeta)$ and then going for an additional time $\tau - \sigma$ to $z(\tau, \zeta)$, which can be written

$$z(\tau, \zeta) = z(\tau - \sigma; z(\sigma, \zeta)). \tag{16}$$

It thus follows from Eq. (15) that

$$\sin[z(\tau; \zeta)] = \frac{\cosh[\alpha(\tau - \sigma)]\sin[z(\sigma; \zeta)] - \sinh[\alpha(\tau - \sigma)]}{\cosh[\alpha(\tau - \sigma)] - \sinh[\alpha(\tau - \sigma)]\sin[z(\sigma; \zeta)]}, \tag{17}$$

which, when solved for $\sin[z(\sigma; \zeta)]$ by algebraic manipulation, gives

$$\sin[z(\sigma; \zeta)] = \frac{\sinh[\alpha(\tau - \sigma)] + \cosh[\alpha(\tau - \sigma)]\sin z(\tau; \zeta)}{\cosh[\alpha(\tau - \sigma)] + \sinh[\alpha(\tau - \sigma)]\sin z(\tau; \zeta)}. \tag{18}$$

The second equation of the Hamiltonian system above can be integrated directly to give

$$c(\tau, z) = c_0 \exp\left\{-\alpha \int_0^{\tau} \sin[z(\sigma; \zeta)]\, d\sigma\right\}, \tag{19}$$

which, upon substitution of Eq. (18) gives

$$c(z, \tau) = c_0 \exp\left\{-\alpha \int_0^{\tau} \frac{\tanh[\alpha(\tau - \sigma)] + \sin z(\tau; \zeta)}{1 + \tanh[\alpha(\tau - \sigma)]\sin z(\tau; \zeta)}\, d\sigma\right\}. \tag{20}$$

The integration in Eq. (20) can be carried out to give

$$c(z, \tau) = \frac{c_0}{\cosh(\alpha\tau) + \sinh(\alpha\tau)\sin z}, \tag{21}$$

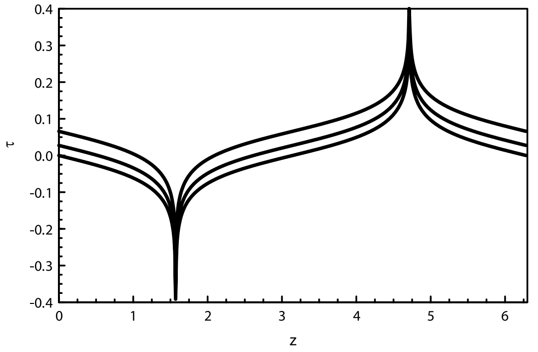

FIG. 1. Plot of the characteristic curves, z versus τ, from Eq. (15). The temperature maximum and minimum are at $\pi/2$ and $3\pi/2$. The top, center, and bottom curves have values of ζ equal to $\pi/3$, $\pi/6$, and 0, respectively.

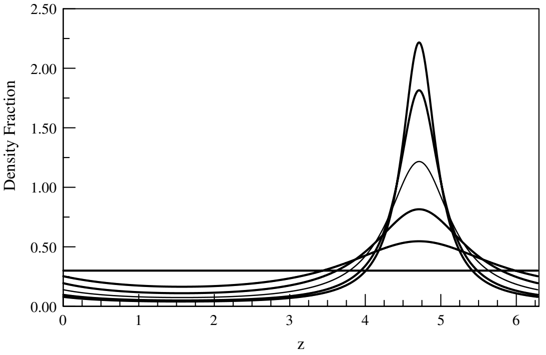

FIG. 2. Plot of density fraction versus coordinate $c(z, \tau)$ from Eq. (21) for $c_0 = 0.3$. The curves are plotted for $\alpha\tau$ values of 0, 0.6, 1.0, 1.4, 1.8, and 2.0 for the flat curve through the most peaked curve, respectively. The sinusoidal temperature field has a temperature maximum at $z = \pi/2$ and a temperature minimum at $z = 3\pi/2$.

where for the present problem $c_0(\zeta) = c_0$ and where z has been substituted for $z(\tau, \zeta)$ in the solution. The solution for c is plotted in Fig. 2 for a relatively large value of α, as is sometimes found in particulate suspensions [13]. Note that Eq. (21) has been derived assuming the nonlinear term and the effects of mass diffusion can be ignored; as such, its validity is restricted to short times when $\alpha\tau \ll 1$, where diffusion is negligible and where $c_0 \ll 1$. Under these conditions it is not difficult to show that the density fraction can be approximated as

$$c(z, \tau) \simeq c_0[1 - \alpha\tau \sin z], \tag{22}$$

so that for short times, the profile of the density fraction is sinusoidal in space.

At the opposite extreme, when τ is long, a steady state is reached where thermal diffusion is counterbalanced by mass diffusion, so that $dc/d\tau = 0$, and Eq. (3) becomes an ordinary differential equation. A first integral of Eq. (3) is $\alpha c \cos z + \frac{dc}{dz} = \Gamma$, where Γ is a constant, which, when evaluated at $z = 3\pi/2$, where both $\cos z$ and dc/dz can be taken as zero, gives the value of Γ as 0. A second integration of Eq. (3) gives $c(z, \tau)$ as a constant times an exponential function of $\sin z$, which, when normalized over the range 0 to 2π, gives

$$c(z, \tau \rightarrow \infty) = \left[\frac{c_0}{I_0(\alpha)}\right] e^{-\alpha \sin z}, \tag{23}$$

where I_0 is a modified Bessel function.

Direct integration of Eq. (21) over z shows that the density fraction conservation law given by Eq. (6) is obeyed. Additionally, the solution given by Eq. (21) shows that for $\alpha > 0$ the density fraction of the first species increases in the region centered at $z = 3\pi/2$, the cold region of the grating. It is easy to see that under a reversal of the sign of α, from a positive to a negative quantity, Eq. (21) becomes $c(z, \tau) = c_0[\cosh(|\alpha|\tau) + \sinh(|\alpha|\tau) \times \sin(z - \pi)]^{-1}$, which shows that the peak in the density fraction profile is translated unchanged in shape to the high temperature region of the grating centered at $\pi/2$, as is well known. The identical property of translation in space under a reversal of the sign of α is found for Eq. (23), as well.

The derivation of Eq. (21), which provides a rigorous description of the density fraction spatial profile for the Ludwig-Soret effect, has been given under the assumption that mass diffusion and the nonlinear contribution to the Ludwig-Soret effect can be ignored—both conditions being valid approximations for small τ. The derivation of Eq. (22) shows that for small $\alpha\tau$, the first Fourier component of the density fraction distribution in space grows linearly in time as $\alpha\tau = T_0 K^2 D' t$, which suggests an experimental method for determining the thermal diffusion factor. The long time solution to Eq. (3), where diffusion is included, can be expanded for small α, which most commonly obtains for solvent mixtures, to give an expression that is in agreement with those used previously to determine Soret coefficients experimentally [9]. In addition to giving an exact solution to the linear problem, the mathematical method described here provides an approach to solution to the nonlinear Ludwig-Soret problem: although the method yields a Hamiltonian system that is both coupled and nonlinear in $c(z, t)$, it forms the basis of a numerical procedure for uncovering the nonlinear dynamics of thermal diffusion. For large values of $\alpha\tau$ the linear solution given here quickly becomes unbounded and demands that on a long time scale the nonlinearity, which produces shocklike discontinuities in the spatial profile of the density fraction, be treated fully.

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