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Kinetics of the Soret effect: Transient in the transport process

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A Green's function is given for the canonical form of the thermodiffusion problem. The analytical and numerical solutions obtained for an initially homogeneous mixture reveal that the process at the boundaries is enhanced during the initial phase. This has to be related to the observations made by Tanner [Trans. Faraday Soc. **23**, 75 (1927)] that the concentration change is "extremely rapid" at the boundaries. Impact on liquid-alloy crystallization is briefly analyzed.

I. INTRODUCTION

The solution of the phenomenological equations of thermodiffusion have been discussed in detail by de Groot.[1] So as to obtain tractable solutions he made some approximations, giving rise to the well-known result that, in a binary mixture between a cold and a hot plate separated by distanced L, the evolution towards the steady-state concentration distribution is established with a characteristic time of $\Theta = L^2/\pi^2 D$, where D is the isothermal diffusion coefficient. The coefficient D is generally around 10^{-5} cm^2 s^{-1}, thus Θ is large.

However, Tanner[2] observed with an optical method that "an extremely rapid concentration change" occurred near the walls of his cell. Thomaes[3] has shown by an approximate Fourier expansion of the solution that the gradient of concentration near the boundaries should behave, at the very beginning of that process, differently than in the relaxation phase, but quantitative results were affected by the approximation.

Such a behavior could be evaluated under microgravity conditions, thus avoiding remixing current induced by density gradients. This transient phenomenon, if its characteristic time is actually very small, could be of technological importance if it appears at the solid boundary of a crystal growing from the melt. If the motions in the liquid phase are oscillatory this behavior could also contribute to striations within the crystal.

The Soret coefficient measurement (SCM experiment[4]) will be launched on the "EURECA" (European Retrievable Carrier) automatic platform of ESA by the U.S. Space Shuttle in 1991 and recovered after six months. In this investigation, the thermodiffusion process will be performed on 20 binary organic and electrolytic mixtures with a good level of microgravity (10^{-5} g). An analysis of the samples will be performed on earth after retrieval. The SCM experiment will be monitored by measuring the electromotive force between electrodes in a cell containing a silver nitrate aqueous solution. The present paper relates parts of the preparatory work performed in order to understand the kinetics of the Soret phenomenon.

II. CANONICAL EQUATIONS FOR TRANSPORT PROBLEMS

We shall consider that the components of an incompressible, nonreacting binary mixture are in a nonconvective state near thermodynamic equilibrium.[5] Then, if N_1 is the mass fraction of one of the two components, the continuity equation is

$$\delta_t N_1 + \bar{\nabla}\cdot\mathbf{J}_1 = 0 \tag{1}$$

and the associated transport flux $\mathbf{J}_1$ is given by[6]

$$\mathbf{J}_1 = -D_{12}\bar{\nabla}N_1 - N_1(1-N_1)D'_{12}\bar{\nabla}T \;, \tag{2}$$

where T is the temperature and D_{12} and D'_{12} are the isothermal diffusion and thermodiffusion coefficients of component (1) in (2). The same equations hold for N_2 but with $D'_{12} = -D'_{21}$. Therefore the subscripts 1 and 2 will not be written anymore and the quantities will refer to component 1 (the solute) and D' will be positive when the solute migrates towards the cold side. The values of D' for the organic mixtures are 2 or 3 orders of magnitude smaller than the isothermal diffusion coefficient[7] so that the chemical separation that is obtained with a temperature difference between cold and hot plates of about 10 K remains small. In this situation, the phenomenological coefficients in the expression of the fluxes can be considered constant. In particular, the temperature profile in a one-dimensional geometry with conducting walls will be linear at steady state. The temperature field will be considered steady during the concentration profile establishment because the Lewis number (defined as the ratio of Prandtl to Schmidt numbers: $\mathcal{N}_{\mathrm{Le}} = \mathcal{N}_{\mathrm{Pr}}/\mathcal{N}_{\mathrm{Sc}} = D/K$, where K is the thermal diffusivity) is of the order of 10^{-2} for organic mixtures and of 10^{-3} for metallic melts.

For small mass fractions N of the studied component (solute) we may thus express the divergence of the flux by (see Refs. 1 and 6, for example)

$$\bar{\nabla}\cdot\mathbf{J}_1 = -D(\bar{\nabla}^2 N + \mathbf{S}\cdot\bar{\nabla}N) \;, \tag{3}$$

where the coefficient $\mathbf{S}$ that we define as

$$\mathbf{S}=(1-N_0)(D'/D)\bar{\nabla}T \tag{4}$$

is considered constant. In Eq. (4), N_0 is the mass concentration of the solute in the initially homogeneous mixture and D'/D is the Soret coefficient (of solute in solvent).

At the boundaries, the continuity equation is no more valid. Two limiting situations can be considered: absorbing walls (where $N=0$) and impervious—or "reflecting"—walls (where $\mathbf{J}\cdot\mathbf{n}=0$, $\mathbf{n}$ being a vector normal to the surface).

In pure diffusion ($\mathbf{S}=0$) the elimination of $\mathbf{J}$ or N between Eqs. (1) and (2) with previous assumptions gives, respectively,

$$\partial_t N-D\bar{\nabla}^2 N=0 \tag{5}$$

and

$$\partial_t \mathbf{J}-D\bar{\nabla}^2\mathbf{J}=-D\bar{\nabla}\times(\bar{\nabla}\times\mathbf{J})=\mathbf{0}\ . \tag{6}$$

This "canonical" form may be obtained also for thermodiffusion, if $\mathbf{S}$ is assumed constant, using the preliminary transformation

$$\begin{bmatrix} N^*(\mathbf{r},t) \\ \mathbf{J}^*(\mathbf{r},t) \end{bmatrix}=f(\mathbf{r}-\mathbf{a},t-t_0)\begin{bmatrix} N(\mathbf{r},t) \\ \mathbf{J}(\mathbf{r},t) \end{bmatrix}\ , \tag{7}$$

where $\mathbf{a}$ is an arbitrary origin for the space vector $\mathbf{r}$ and where f is defined by

$$f(\mathbf{r},t)=\exp(\mathbf{S}^2Dt/4+\mathbf{S}\cdot\mathbf{r}/2)\ . \tag{8}$$

Then

$$\partial_t\begin{bmatrix} N^* \\ \mathbf{J}^* \end{bmatrix}-D\bar{\nabla}^2\begin{bmatrix} N^* \\ \mathbf{J}^* \end{bmatrix}=\begin{bmatrix} 0 \\ -D\bar{\nabla}\times(\bar{\nabla}\times\mathbf{J}^*) \end{bmatrix}\ . \tag{9}$$

The right-hand side (rhs) of Eq. (9) vanishes when $\bar{\nabla}N$ remains parallel to $\mathbf{S}$ (as in the one-dimensional problem). The previous conditions are preserved by the transformation (7). So, the four problems of diffusion and thermodiffusion with absorbing or reflecting boundaries that have been defined above, may be reduced to the canonical problem

$$\partial_t F-D\bar{\nabla}^2 F=0\ ,$$

with, at the boundaries

$$\mathbf{F}\cdot\mathbf{n}=0\ . \tag{10}$$

(For absorbing boundaries F will be N or N^* and for reflecting boundaries $\mathbf{F}$ will be the vector $\mathbf{J}$ or $\mathbf{J}^*$).

III. SOLUTION OF THE CANONICAL PROBLEM

The problem (10) will be solved independently of the initial conditions. For an infinite medium the solution is

$$F(\mathbf{r},t)=\langle G(\mathbf{r}-\mathbf{r}_0,t-t_0)F(\mathbf{r}_0,t_0)\rangle_{\mathbf{r}_0}\ , \tag{11}$$

where the angular brackets are placed for integration on the space variable $\mathbf{r}_0$, and where the Green's function is the normalized Gaussian distribution of standard deviation $(Dt)^{1/2}$ defined by

$$G(\mathbf{r},t)=(4\pi Dt)^{-n/2}\exp[-\mathbf{r}^2/(4Dt)] \tag{12}$$

(n being the number of spatial dimensions considered in the problem).

The similitude with Brownian motion is well known:[8] G is the probability that a particle is moved from $\mathbf{r}_0$ to $\mathbf{r}$ during a time $t-t_0$. In particular

$$\lim_{t\to 0+} G(\mathbf{r}-\mathbf{r}_0,t-t_0)=\delta(\mathbf{r}-\mathbf{r}_0)\ , \tag{13a}$$

$$\lim_{t\to +\infty} G(\mathbf{r}-\mathbf{r}_0,t-t_0)=0\ , \tag{13b}$$

and

$$\langle G\rangle_{\mathbf{r}}=\langle G\rangle_{\mathbf{r}_0}=1\ . \tag{13c}$$

When absorbing barriers are introduced, the symmetry expressed by the first equality of Eq. (13c) is broken. This problem can easily be solved in a one-dimensional geometry with use of the method of images. One gets, if x is the space variable,

$$F(x,t)=\langle P(x,x_0,t)F(x_0,t_0)\rangle_{x_0}\ , \tag{14}$$

where the Green's function is now given by

$$P(x,x_0,t)=P_+(x,x_0,t)-P_-(x,x_0,t) \tag{15}$$

and $P_\pm$ are given for a semi-infinite medium extending between $x=0$ and $x=+\infty$ by

$$P_\pm(x,x_0,t)=G(-x_0\pm x,t)\ . \tag{16}$$

When the medium extends between $x=0$ and $x=L$, results (14) and (15) apply with the infinite expansion

$$P_\pm(x,x_0,t)=\sum_{p=-\infty}^{+\infty} G(-x_0\pm x+2pL,t)\ . \tag{17}$$

From the following property

$$\pm\partial_x P_\pm(x,x_0,t)=-\partial_x P_\pm(x,x_0,t)\ , \tag{18}$$

with Eq. (15) and absorption boundary conditions we obtain

$$\partial_x F=\langle(P_+ + P_-)\partial_{x_0}F > x_0\ . \tag{19}$$

This could have been found by the method of images also, using the fact that if F is submitted to absorption conditions at the boundary, $\delta_x F$ will be submitted to reflection conditions.

IV. ANALYTICAL SOLUTIONS FOR THE THERMODIFFUSION PROBLEM

A. Evolution of operator

In the infinite medium, the result (11) can be used for both N^* and $\mathbf{J}^*$. Turning back to the original variables, we have for the mass concentration N:

$$N(\mathbf{r},t)=\langle G(\mathbf{r}-\mathbf{r}_0+\mathbf{S}Dt,t)N(\mathbf{r}_0,0)\rangle_{\mathbf{r}_0} . \qquad (20)$$

To the pure diffusive process, a drift phenomenon is added that has a constant velocity drift equal to $\mathbf{S}D$.

As can be seen by Eq. (4) this velocity is proportional to the temperature gradient. For a one-dimensional semi-infinite or finite medium with impervious boundaries we have

$$J(x,t)=\exp(-S^2Dt/4-Sx/2)\times\langle (P_+-P_-)\exp(Sx_0/2)J(x_0,0)\rangle_{x_0} . \qquad (21)$$

The concentration distribution can be deduced from Eq. (21) by the continuity equation [Eq. (1)]. The classical Fourier expansion for the finite one-dimensional cell is also deduced from Eq. (21) with the identity:[9]

$$\sum_{p=-\infty}^{+\infty} G(y+2pL,t)=1/(2L)+\frac{1}{2}\sum_{p=-\infty}^{+\infty}\cos(\pi py/L)\exp(-tp^2\pi^2D/L^2) . \qquad (22)$$

B. Behavior of an initially homogeneous mixture

For the semi-infinite medium extending between $x=0$ and $x=+\infty$ the evolution of the flux for an initially homogeneous situation is given by

$$J(x,t)/J_0=\tfrac{1}{2}\mathrm{erfc}[(-x-SDt)/(4Dt)^{1/2}]-\tfrac{1}{2}\exp(-Sx)\mathrm{erfc}[(x-SDt)/(4Dt)^{1/2}] , \qquad (23)$$

where erfc(x) is the "complementary error function" and J_0 is equal to $-N_0SD$.

The flux is equal to J_0 everywhere for $t\to0+$ except at the boundary where it vanishes (the solution found is consistent with the boundary and initial conditions in the sense of distributions[10]). Thus step initial distribution of the flux[11] evolves toward a stationary value that, according to Eq. (23), is zero for S negative and $[1-\exp(-Sx)]$ for S positive. The wall is then enriched in solute coming from an infinitely extended reservoir (thus not leading to a stationary concentration). The solution will be consistent only for finite times and distances from the wall.

To further analyze how this happens we may look at the enrichment rate deduced from Eq. (23) by the continuity equation:

$$\partial_t N/J_0=-2G(x+SDt,t)-(S/2)\exp(-Sx)\mathrm{erfc}[(x-SDt)/(4Dt)^{1/2}] . \qquad (24)$$

The limiting temporal values for the enrichment rate are reported in Table I.

When S is negative, the solute is rejected at infinity. Thus the enrichment rate is negative and tends to zero at finite distances. This rejection starts at the wall. For S positive, the enrichment rate is positive and different from zero at the beginning only at the wall. This may be called the "squashing of solute" onto the wall. Enrichment then proceeds into the bulk by the combined action of retrodiffusion from the wall [first term of Eq. (23)] and thermodiffusion from and to the other regions [second term of Eq. (23)].

TABLE I. The limiting temporal values for the enrichment values for positive and negative values of S.

	$S>0$	$S<0$
$\lim_{t\to0^+}\partial_t N$	$(2+S/2)N_0SD\delta(x)$	$2N_0SD\delta(x)$
$\lim_{t\to+\infty}\partial_t N$	$N_0SDS\exp(-Sx)$	0

Because the second term is of the order S (for $S<0$ only at finite distance, say $-Sx\le1$), the behavior of the enrichment rate is well approximated by

$$\partial_t N=-2J_0G(x+SDt,t) \qquad (25)$$

if $(Dt)^{1/2}$ and $(x+SDt)/(4Dt)^{1/2}$ are small (say much less than 1). Thus for short times the layer defined by

$$x\le2(Dt)^{1/2}-SDt \qquad (26)$$

will be submitted to a squashing-retrodiffusion process.

The time for which this is valid may be estimated saying that the diffusion length $(Dt)^{1/2}$ is much less than the length L of the "infinite" cell. This lead to $t\ll\Theta$ and $x\ll L$. A more precise statement is obtained further below.

V. ESTIMATIONS FOR A FINITE CAVITY WITH IMPERVIOUS WALLS

Computations have been performed for a closed one-dimensional cavity with 300 terms in the Fourier expansion.[11] The spatial variable is reduced by length L of the cell, the time by Θ. The flux and the concentration exhibit a weak dependence on the value of SL when they are reduced, respectively, by the reference flux $-N_0SD$ and by the stationary concentration distribution. The approximation usually performed, the stationary distribution multiplied by the temporal factor $[1-\exp(-t/\Theta)]$, may be obtained considering the first two terms in the Fourier expansion of the solution. This "two-terms" approximation shows no dependence on S.

There is an important discrepancy between this approximation and the exact solution. In this later, the spatial dependence of the evolution of the reduced flux and concentration at the beginning of the process is very pronounced.

The flux evolves from a rectangular distribution to-

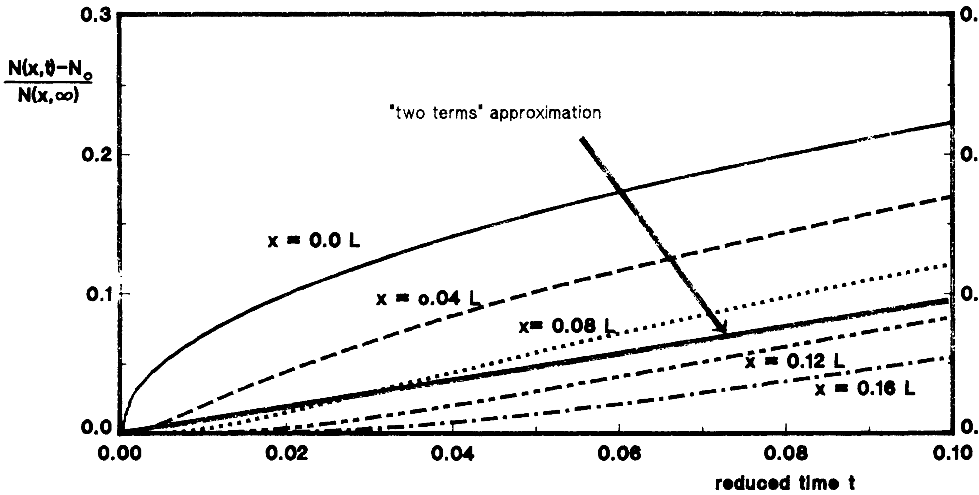

FIG. 1. Evolution of concentration vs time at different depths of the cavity with impervious walls. Concentration is reduced by the stationary distribution and time by the characteristic diffusion time Θ. The enhanced curve shows the approximation that can be used for larger times.

ward zero.[11] The behavior of the reduced concentration distribution $[N(x,t)-N_0]/N(x,\infty)$ is shown in Fig. 1 by its evolution in different points of the cell near the boundary and for small values of the reduced time. The value $SL=0.01$ is taken from μg experiments performed on Sn-Co melts[12] and from ground-based experiments performed on organic mixtures in a flow cell.[13] At $t=0.02\Theta$ already 10% of the chemical separation is reached at the boundaries and only 0.2% at $x=0.16\ L$. The "two-terms" approximation (also shown in Fig. 1) predicts a value of 2% everywhere in the cavity. Thus for short-time intervals after the establishment of the temperature gradient, there is a discrepancy of about 1 order of magnitude between the two models. In the exact approach the effect is lowered in the bulk and enhanced at the impervious boundaries. This can be explained by the squashing of the pure thermodiffusion flux on the walls and by retrodiffusion in the bulk from the boundaries.

During this phase let us now consider a small element of volume located at x_0. A small concentration inhomogeneity drifting with a speed $-SD$, with S positive, during a time δt will be spread by diffusion on an interval of about

$$x_0-SD\delta t\pm(D\delta t)^{1/2} \tag{27}$$

and will thus disappear by diffusion if it has born far enough from the wall. Suppose now that this wall is progressing with a mean velocity v due, for example, to a crystallization process. The time required for the concentration fluctuation to reach the wall will be given by

$$\delta t=x_0/(v+SD)\ . \tag{28}$$

At this time it will be spread between the wall and

$$(D\delta t)^{1/2}=[x_0/(S+v/D)]^{1/2}\ . \tag{29}$$

If this last ratio is small, the concentration inhomogeneity will be squashed nearly completely on the crystallization boundary. Thus the depth l for which concentration inhomogeneity may be of importance for crystal growth is about

$$l=(S+v/D)^{-1} \tag{30}$$

and the corresponding time for the migration of the fluctuation is

$$\delta t=\Theta[\pi D/(v+SD)]^2/L^2\ . \tag{31}$$

Typical values for v and D are, respectively, 10^{-4} and $10^{-5}\ \mathrm{cm^2\,s^{-1}}$. Thus l is about 0.1 cm and δt about $(0.1/L^2)\ \Theta$, L being expressed in cm, and will not be very sensitive to S for this amplitude of the velocity of crystallization.

The initial phase will be of importance for most practical situations in crystal growth because the effect is of short characteristic time. Even if the component is rejected from the wall, or only partially absorbed, the high variation of concentration by the Soret effect in a very short time may significantly affect the other physical processes involved in the crystallization. Such a variation may be induced for example by a temperature perturbation.

VI. CONCLUSIONS

The Green's function for one-dimensional diffusion and thermodiffusion problems have been written for reflecting or absorbing frontiers. It is valid when frontiers are moving. Analytical and numerical solutions deduced for the one-dimensional geometry reveals that up to some percents of the diffusion characteristic time, a "drift" process, in which the concentration change at the walls is highly enhanced, is governing the evolution of concentration distribution. This should be taken into account especially in crystallization and double diffusively instability problems.

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