

# THERMAL DIFFUSION IN IONIZED GASES AND PLANETARY AND SOLAR PROCESSES

Thermal diffusion, which has been presumed to be an important process in ionized gases such as those that occur in planetary ionospheres and in stellar interiors, is recalculated, taking into account two effects that have previously been ignored. The first effect is that quantum mechanics must be used to calculate collision cross sections at high temperatures as well as at low. The second effect is that the sea of charges surrounding two moving charges does not instantaneously follow the relative motion of the two charges. In ionized gases that are characteristic of stellar interiors, the newer estimates of thermal diffusion differ substantially from the estimates produced by the older theory.

## INTRODUCTION

Thermal diffusion is ordinarily a secondary effect; that is, whereas gradients in concentration and temperature result in fluxes either of molecules or of energy, thermal diffusion describes the process whereby a gradient in temperature produces a molecular flux. If we define  $x_i$  as the mole fraction and  $j_i$  as the molecular flux of component  $i$  ( $i = 1, \dots, N$  in a multicomponent mixture),  $T$  as the temperature, and  $F_i$  as the external force (as distinguished from intermolecular force or the total body force) acting on component  $i$ , a Stefan-Maxwell equation may be written relating the molecular fluxes to  $x_i$ ,  $T$ , and  $F$ . Thus,

$$\nabla x_i - \frac{x_i m_i}{kT} F_i \approx \sum_{l=1}^N \left[ \frac{1}{n(D_{il})} (x_i j_l - x_l j_i) \right] - x_i x_l \alpha_{il} \nabla \ln T, \quad (1)$$

where  $k$  is the Boltzmann constant,  $m_i$  is the molecular weight,  $n$  is the number of molecules per unit volume,  $(D_{il})$  is the binary diffusion coefficient, and  $\alpha_{il}$  is the binary thermal diffusion factor. The advantage in writing the flux equation in this form rather than in the usual Fick's law form is that for gases at moderate pressure, the binary diffusion coefficient and thermal diffusion factor are functions only of the two-body interactions. Also, in the steady state (i.e., where each of the molecular fluxes vanishes) it is easily seen that a temperature gradient induces a concentration gradient, and vice versa. The proportionality factor (i.e., the thermal diffusion factor) is small ordinarily and was undetected experimentally for many years. In fact, for Maxwellian molecules (a not unreasonable model), the components of  $\alpha_{il}$  vanish identically, and the earliest gas kinetic theories, which assumed this model implicitly or explicitly,<sup>1</sup> consequently missed predicting the effect entirely. Nevertheless, thermal diffusion found its

niche in the technology for isolating hydrogen and uranium isotopes developed during and after World War II.

However, until a seminal paper by Sidney Chapman<sup>2</sup> was published, it was not suspected that the thermal diffusion factors in ionized gases were enormous and that thermal diffusion could very well be the dominant process determining the steady-state distributions and fluxes of ions induced by thermal gradients. Since then, there have been many discussions incorporating this effect into the theories of planetary atmospheres, solar coronas, and the evolution of white dwarf stars. The theories have not been completely successful because there has been some disagreement between the observed and the theoretically predicted ion concentration profiles and fluxes in planetary atmospheres<sup>3</sup> and solar coronas.<sup>4</sup> The discrepancies and the fact that thermal diffusion is so sensitive to details of the molecular force field<sup>1</sup> suggest that there should be a more careful look at this process in ionized gases. The presentation that follows summarizes a collaborative effort between the author and E. A. Mason of Brown University<sup>5</sup> that was initiated to investigate this very point.

## THE QUANTAL AND THE DYNAMIC SHIELDING CORRECTION

It quickly became evident that the use of a classical kinetic theory of transport processes in plasmas<sup>2,6</sup> could be a source of trouble. The classical theory assumes that the coulomb interaction between two isolated ions is modified by the surrounding sea of charges and that the interaction can be replaced by the Debye or shielded coulomb potential,  $\phi_D(r)$ , defined by

$$\phi_D(r) = \frac{Z_1 Z_2}{r} e^{-r/\lambda_D}. \quad (2)$$

Here  $Z_1$  and  $Z_2$  are the charges on ions 1 and 2,  $r$  is the distance separating ions 1 and 2, and  $\lambda_D$  is the



Debye shielding length, which is a function of  $T$ , the electronic charge,  $e$ , and the number of electrons per unit volume,  $n_e$ , expressed by

$$\lambda_D = (kT/4\pi e^2 n_e)^{1/2}. \quad (3)$$

Two assumptions are made: (a) that classical mechanics is adequate for calculating the trajectory of two colliding ions, and (b) that the interaction between the two ions is given by Eq. 2. Both assumptions have been challenged but, surprisingly, not for the theory of thermal diffusion.

One requirement of assumption (a) is that classical trajectories be well defined; this, in turn, requires that the orbital angular momenta that contribute effectively to a collision be much greater than the lowest observable quantum of angular momentum. This requirement may be shown<sup>7</sup> to be equivalent to the requirement that

$$\sigma^{1/2}(T) \gg \lambda, \quad (4)$$

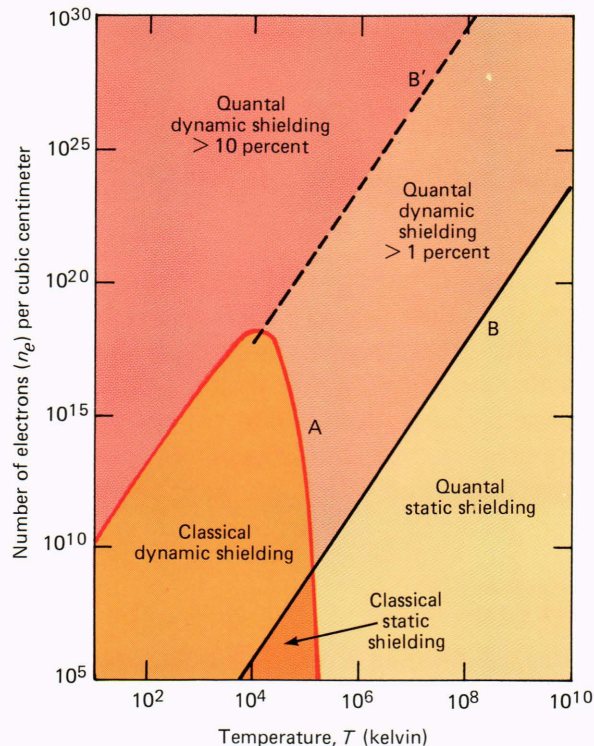
where  $\sigma^{1/2}$ , the square root of the effective cross section for the collision, is a measure of the effective range of the potential. The effective cross section is generally a decreasing function of energy (i.e., temperature) but is always finite.

The de Broglie wavelength,  $\lambda$ , is defined by

$$\lambda = \frac{h}{2\pi(2kTm)^{1/2}}, \quad (5)$$

where  $h$  is Planck's constant and  $m$  is the relative mass of the colliding pair. At low energy (temperatures), Eq. 4 will always be violated for all potentials, and classical mechanics breaks down. At high energy,  $\lambda$  decreases as  $T^{-1/2}$  and Eq. 4 will be satisfied for interactions whose effective ranges are relatively insensitive to temperature. It is a peculiarity of the Debye potential that at high energy,  $\sigma^{1/2}(T)$  decreases with  $T$  more rapidly than  $\lambda$  does, leading to the breakdown of the inequality of Eq. 4. It follows then that classical mechanics can be used to describe collisions of particles interacting with the Debye potential for only a finite intermediate range of energies. We carried out quantum and classical mechanical calculations of  $\alpha_{ij}$  using methods that were found to be successful in other applications.<sup>8</sup> Curve A in Fig. 1 is the locus of points where the difference between the quantum and classical approximations exceeds 1 percent in a hydrogen plasma.

Assumption (b) states that the effective force between two of the ions in an ionized gas is the coulomb force modified by a partial shielding of the ions by all the charges between them. Since the Debye potential is the form taken by the effective potential under equilibrium conditions, assumption (b) is tantamount to requiring that the distribution of the surrounding charges



**Figure 1**—Comparison of quantum and classical mechanical calculations of the thermal diffusion factor. Curve A is the locus of points where the error due to the neglect of quantum effects equals 1 percent. Curves B and B' are the loci of points for which the dynamical shielding effects equal 1 percent and 10 percent.

relax instantaneously as the configuration of the two ions changes. We replaced assumption (b) (which is sometimes called the static shielding approximation) by a dynamic shielding approximation that allows the surrounding ion sea to lag somewhat in its response to motions of the two ions considered here. In the kinetic theory of transport in ionized gases,<sup>9</sup> the dynamic shielding approach is accomplished by replacing the Debye potential by a frequency-dependent potential; this is equivalent to replacing the static polarization or dielectric constant by frequency-dependent functions. Following this procedure,<sup>9</sup> corrections to thermal diffusion factors were calculated<sup>5</sup> to plot curves B and B' in Fig. 1. The curves represent, respectively, the loci of points where the contribution due to dynamic shielding equals 1 percent and 10 percent.

### CONSEQUENCES IN IONOSPHERIC AND SOLAR PHYSICS

Although in an  $n_e$ - $T$  plot the region is rather small where the classical and static shielding approximations are valid simultaneously (cf. Fig. 1), it includes most planetary atmospheres and the solar corona. Consequently, the calculations carried out on ion distributions in the Venus ionosphere<sup>3</sup> are probably valid, and the explanation of anomalous ion distributions must be sought elsewhere. For rather different reasons, expla-



nations of the anomalously low concentration of heavy ions in the corona and the solar wind can be shown to result from more than thermal diffusion alone.

The specific problem in the latter case is that the ratio of helium to hydrogen in the interior of the sun is presumed by some solar physicists<sup>4</sup> to be the same as the primordial helium-to-hydrogen ratio,  $\approx 0.048$ . The motion in the chromosphere and in the outer convection zone ( $0.86$  to  $1.0$  sun radius ( $R_{\odot}$ )) is observed to be quite turbulent and therefore should provide an efficient mixing process for the ions in that region (see Fig. 2). The region below  $0.86 R_{\odot}$  is expected to be characterized by laminar flow on the basis of Reynolds numbers calculated for gas viscosities approximated by the classical kinetic theory for ionized gas. Although the ion separations in the steady state are predicted to be more than enough to explain this phenomenon, the times required to reach the steady state tend to be much shorter than the lifetime of the sun! A short calculation in the classical approximation<sup>10</sup> showed that during an elapsed time of  $4.5 \times 10^9$  years (the estimated age of the earth) the helium concentration at the base of the convection zone would have been reduced by 10 percent, which is not enough to explain the observed value. Inserting the revised kinetic theory does not help matters because a quick back-of-the-envelope calculation shows that the introduction of quantal and dynamic shielding effects reduces the estimated depletion to 1 percent. In general, then, thermal diffusion is a much slower process in stellar interiors than was predicted by the classical kinetic theory. Moreover, since the viscosity changes in the same manner as the diffusion coefficient, the classical approximation overestimates viscosity in the interior of the sun by a factor of 5 to 10. Therefore, the Taylor numbers used to predict the onset of circulation and the Reynolds numbers used to predict the onset of turbulence are seriously underestimated. All of these enumerated effects tend to maintain the helium-to-hydrogen ratio in the interior of the sun at a constant value.

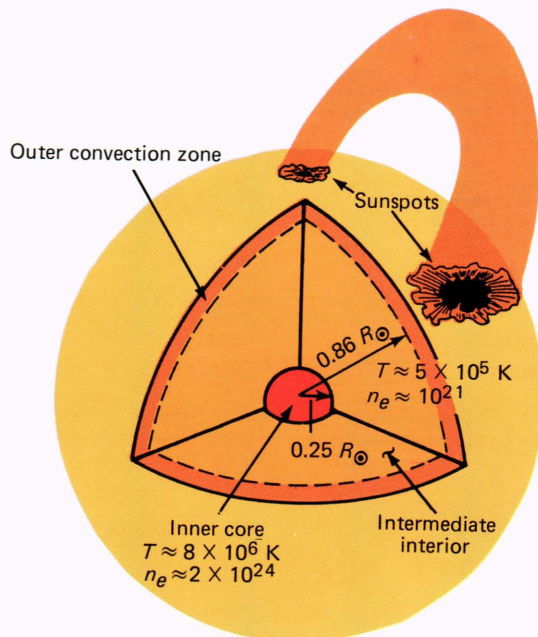
In summary, our calculations confirm the importance of thermal diffusion in planetary atmospheres and discount its importance in solar and stellar physics.

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## THE AUTHOR

LOUIS MONCHICK, a member of the Principal Professional Staff and the Milton S. Eisenhower Research Center, joined APL in 1957. In addition to a joint appointment as lecturer in the Department of Chemical Engineering, he has held appointments as part-time visiting professor in chemistry (1968) and Parsons professor in chemistry (1976) and in chemical engineering (1981), all at The Johns Hopkins University. He has also been a visiting scientist at the Universities of Bielefeld (1979) and Leiden (1980). His research interests are the kinetic theory of gases and gas transport properties, molecular collisions, diffusion-controlled reactions, and spectral line shapes.



**Figure 2**—Schematic diagram of the sun. The chromosphere (marked by sunspots) and corona (marked by luminous plumes) occupy a region outside the solar radius ( $R_{\odot}$ ) and are very turbulent. The outer convective zone occupies a region within but greater than 86 percent of the solar radius and is thought to be very turbulent. The intermediate interior occupies a region that is less than 86 percent but greater than 25 percent of the solar radius and is thought to be very quiet.

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