

KINETIC THEORY OF THE INTERDIFFUSION COEFFICIENT IN DENSE PLASMAS *

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INTRODUCTION

Ionic diffusion in dense plasma mixtures has been of interest recently for a number of reasons. In astrophysics, diffusion plays a central role in understanding the distribution of heavy elements in the atmospheres of White Dwarf stars.¹ The performance of multi-layer x-ray mirrors should be affected by diffusion, and the evaporation rate of metal "chunks" injected into the fuel of an ICF capsule by hydrodynamic instabilities is controlled by the diffusion coefficient.

In all of these applications, the plasmas can be very dense and estimates based upon the Spitzer formula² are often inadequate. In fact, naive applications of Spitzer's theory can lead to negative diffusion coefficients. Simple modifications, such as placing a "floor" on the value of the Coulomb logarithm³, can eliminate such unphysical results, but they are untested under these conditions.

The interdiffusion coefficients in Binary Ionic Mixtures (two species of point ions in a uniform neutralizing background) have been calculated recently using molecular dynamics techniques by Hansen et al.⁴ and by Pollock.⁵ These calculations can provide useful benchmarks for theoretical evaluations of the diffusion coefficient in dense plasma mixtures. This paper gives a brief description of a kinetic theoretic approximation to the diffusion coefficient which generalizes Spitzer to high density and is in excellent agreement with the computer simulations.

DIFFUSION IN A BIM

As mentioned above, a Binary Ionic Mixture is a model of a plasma mixture with two species of classical point ions immersed in a uniform neutralizing background. The charge and mass of ion species " σ " are indicated by $Z_\sigma e$ and m_σ , respectively. Similarly, the number and mass densities are n_σ and $\rho_\sigma = m_\sigma n_\sigma$. The corresponding total densities are $n = n_1 + n_2$ and $\rho = \rho_1 + \rho_2$.

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The strength of the Coulomb coupling among the ions is measured by the parameter,

$$\Gamma = \frac{e^2}{r_0 k_B T}$$

where T is the temperature and r_0 is the ion sphere radius

$$\frac{4\pi r_0^3}{3} = 1/n$$

There are two characteristic plasma frequencies in a BIM. One is the Vlasov plasma frequency defined by

$$\omega_p^2 = \omega_1^2 + \omega_2^2 = \frac{4\pi n_1 Z_1^2 e^2}{m_1} + \frac{4\pi n_2 Z_2^2 e^2}{m_2} = 4\pi n e^2 \overline{Z^2/m} \quad (1)$$

The other is the so-called "hydrodynamic" plasma frequency defined by

$$\bar{\omega}_p^2 = 4\pi n e^2 \overline{Z^2/m} \leq \omega_p^2 \quad (2)$$

In the above, barred quantities are number weighted averages,

$$\bar{A} = c_1 A_1 + c_2 A_2 \quad (3)$$

where $c_\sigma = n_\sigma/n$ is the number concentration. The corresponding mass concentration is $X_\sigma = \rho_\sigma/\rho$.

The rate at which concentration fluctuations dissipate in a mixture is governed by the interdiffusion coefficient, D, which linearly relates mass fluxes to gradients in the mass concentration. Specifically, if the center-of-mass velocity field, \vec{u} , is defined by

$$\vec{u}(\vec{r}, t) = \sum_{\sigma=1}^2 X_\sigma(\vec{r}, t) \vec{u}_\sigma(\vec{r}, t) \quad (4)$$

where \vec{u}_σ is the velocity field of species " σ ", then the mass flux of " σ " is

$$\vec{J}_\sigma(\vec{r}, t) = \rho_\sigma(\vec{r}, t) (\vec{u}_\sigma(\vec{r}, t) - \vec{u}(\vec{r}, t)) \quad (5)$$

and the interdiffusion coefficient is defined by the relationship,⁶

$$\vec{J}_\sigma(\vec{r}, t) = -\rho(\vec{r}, t) D \vec{\nabla} X_\sigma(\vec{r}, t) \quad (6)$$

As is the case with many other transport coefficients, D can be related to an equilibrium time correlation function. In particular, it can be shown that

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$$D = \frac{c_1 c_2}{S_{cc}(k=0)} \int_0^{\infty} dt v_D(t) \quad (7)$$

where

$$v_D(t) = \frac{1}{3Nc_1c_2} \langle \vec{v}_D(t) \cdot \vec{v}_D(0) \rangle_0 \quad (8)$$

is the autocorrelation function for the (microscopic) diffusion velocity

$$\vec{v}_D(t) = c_2 \sum_{i \in 1} \vec{v}_i(t) - c_1 \sum_{i \in 2} \vec{v}_i(t) \quad (9)$$

The concentration structure factor, $S_{cc}(k)$, is defined in terms of the partial structure factors, $S_{\sigma\sigma}(k)$, as

$$S_{cc}(k) = c_1 c_2 [c_2 S_{11}(k) + c_1 S_{22}(k) - 2\sqrt{c_1 c_2} S_{12}(k)] \quad (10)$$

In the low- k limit, S_{cc} is related to the Gibbs free energy through

$$S_{cc}(k=0) = Nk_B T / \frac{\partial^2 G}{\partial c_1^2} \quad (11)$$

The appearance of the factor $c_1 c_2 / S_{cc}(k=0)$ in the expression for D , therefore, accounts for the fact that diffusion is really driven by gradients of the chemical potential, not density. For neutral gases, this factor reduces to unity for all concentrations in the low density limit. For charged particles, however, $c_1 c_2 / S_{cc}$ remains concentration dependent even in the weak-coupling limit. This may be seen by using the Debye-Huckel estimates of the partial structure factors to obtain

$$c_1 c_2 / S_{cc}(k=0) \rightarrow \bar{z}^2 / \bar{z}^{\prime 2} \quad (12)$$

which is greater than unity whenever $c_1 c_2 \neq 0$.

THE ENHANCEMENT FACTOR AND THE AMBIPOLAR FIELD

As seen in the previous section, the long-range nature of the Coulomb potential leads to an enhancement of ion diffusion in a binary mixture, even in the low-density limit. In this section it will be shown that an identical result follows from the usual Boltzmann theory of diffusion, provided the ambipolar field of the electron background is taken into account.

If temperature gradients are neglected, the standard Boltzmann approach gives⁸

$$\vec{j}_1 = - \frac{n_1 n_2 n^2}{\rho} D_0 \vec{d}_1 \quad (13)$$

where D_0 is the Spitzer estimate of the diffusion coefficient and \vec{d}_1 is

$$\vec{d}_1 = \frac{1}{n} (\vec{v}n_1 - \frac{Z_1 n_1 e}{k_B T} \vec{E}) + \frac{X_1}{p} \left(\sum_{\sigma=1}^2 Z_{\sigma} n_{\sigma} e \vec{E} - \vec{v}p \right) \quad (14)$$

The ambipolar field is \vec{E} and the pressure is given by $p = nk_B T$. By assuming the system is mechanically stable,

$$\vec{v}p = (Z_1 n_1 + Z_2 n_2) e \vec{E}, \quad (15)$$

and that it is charge-neutral over hydrodynamic scale-lengths,

$$Z_1 \vec{v}n_1 = - Z_2 \vec{v}n_2, \quad (16)$$

it is straight-forward to find

$$\vec{d}_1 = -\rho \frac{k_B T}{Z_1} D_0 \vec{v}X_1 \quad (17)$$

Comparison with (12) shows that, at least in the low-density limit, the thermodynamic factor, $c_1 c_2 / S_{cc}(k=0)$, may be thought of as an enhancement of the ion diffusion due to the ambipolar electric field of the electrons.

KINETIC THEORY FOR THE TIME-CORRELATION FUNCTION

Any time correlation function may be expressed in terms of the correlations of the phase space densities

$$f_{\sigma}(\vec{r}p, t) = \sum_{i \in \sigma} \delta(\vec{r} - \vec{r}_i(t)) \delta(\vec{p} - \vec{p}_i(t)) \quad (18)$$

If δf_{σ} represents the deviation of f_{σ} from its equilibrium average value, then the phase-space correlation functions are

$$C_{\sigma\sigma'}(\vec{r}-\vec{r}', t | \vec{p}\vec{p}') = \langle \delta f_{\sigma}(\vec{r}p, t) \delta f_{\sigma'}(\vec{r}'\vec{p}', 0) \rangle_0 \quad (19)$$

It is usually more convenient to deal with the transformed functions

$$\bar{S}_{\sigma\sigma'}(kz; \vec{p}\vec{p}') = \int_0^{\infty} dt e^{izt} \int d^3r C_{\sigma\sigma'}(\vec{r}-\vec{r}', t | \vec{p}\vec{p}') e^{-i\vec{k} \cdot (\vec{r}-\vec{r}')} \quad (20)$$

The diffusion coefficient may be written in terms of these latter functions as

$$D = \frac{c_1 c_2}{S_{cc}} \operatorname{Re} \bar{v}_D(0 + i\eta) \quad (\eta \rightarrow 0^+) \quad (21)$$

where

$$\begin{aligned} \bar{v}_D(z) &= \int_0^\infty dt e^{izt} v_D(t) \\ &= \frac{1}{3} \sum_{\sigma, r} \gamma_\sigma \gamma_r \int d^3 p d^3 p' \bar{S}_{\sigma\sigma'}(k=0, z; \vec{p}\vec{p}') \vec{p} \cdot \vec{p}' \end{aligned} \quad (22)$$

$$\text{with } \gamma_1 = \frac{1}{n_1} \sqrt{\frac{c_2}{n_1}} \text{ and } \gamma_2 = \frac{1}{n_2} \sqrt{\frac{c_1}{n_2}}$$

The transformed phase-space correlation functions obey a kinetic equation of the form

$$\begin{aligned} (z - \frac{\vec{k} \cdot \vec{p}}{m_\sigma}) \bar{S}_{\sigma\sigma'}(kz; \vec{p}\vec{p}') &= \sum_{\sigma'} \int d^3 \vec{p}' \phi_{\sigma\sigma'}(kz; \vec{p}\vec{p}') \bar{S}_{\sigma'}(kz; \vec{p}' \vec{p}') \\ &= i n_\sigma \phi_\sigma(p) [\delta_{\sigma\sigma'} \delta(\vec{p}-\vec{p}') + n_r \phi_r(p') \bar{h}_{\sigma r}(k)] \end{aligned} \quad (23)$$

where $\phi_\sigma(p)$ is the normalized Maxwell-Boltzmann distribution for species σ and $\bar{h}_{\sigma r}(k)$ is related to the radial distribution function through Fourier transformation

$$\bar{h}_{\sigma r}(k) = \int d^3 x e^{i\vec{k} \cdot \vec{x}} (g_{\sigma r}(x) - 1). \quad (24)$$

The operator $\phi_{\sigma r}$ is written as

$$\phi_{\sigma r}(kz; \vec{p}\vec{p}') = -n_\sigma \frac{\vec{k} \cdot \vec{p}}{m_\sigma} \phi_\sigma(p) \bar{c}_{\sigma r}(k) + \bar{H}_{\sigma r}(kz; \vec{p}\vec{p}') \quad (25)$$

which is the sum of a mean-field term involving the direct correlation functions

$$\bar{c}_{\sigma r}(k) = \bar{h}_{\sigma r}(k) - \sum_{\sigma'} \bar{c}_{\sigma\sigma'}(k) \bar{h}_{\sigma' r}(k) \quad (26)$$

and the "memory" function, $\bar{H}_{\sigma r}$, which contains the effects of collisions.

The standard procedure for solving (23) is to expand the momentum dependence of the $\bar{S}_{\sigma\sigma'}$'s in terms of Hermite polynomials, which are a complete set of orthogonal polynomials with Maxwell-Boltzmann weight functions. The Hilbert space defined by these functions is then divided into two subspaces: the "hydrodynamic subspace" spanned by the ten (five for each species) functions corresponding to the hydrodynamically conserved quantities, number, three components of momentum and (kinetic energy,¹⁰ and its complement, the "non-hydrodynamic" subspace. Projecting the kinetic equation onto the "hydrodynamic" subspace then yields a closed set of equations for the hydrodynamic matrix elements of the $\bar{S}_{\sigma\sigma'}$'s. The details of this procedure are well described in the paper by Baus¹¹ and will not be given here.

Applying Baus' method to the problem at hand ultimately yields

$$\bar{v}_D(z) = \frac{1}{3} \bar{v}_2(z) + \frac{2}{3} \bar{v}_1(z) \quad (27)$$

where

$$\bar{v}_2(z) = \frac{\rho k_B T}{n m_1 m_2} \frac{iz(z^2 - \Omega_p^2)}{z^2(z^2 - \omega_p^2) + iz\nu(z)(z^2 - \Omega_p^2)} \quad (28)$$

is the correlation function for the longitudinal component of the diffusion velocity and

$$\bar{v}_1(z) = \frac{\rho k_B T}{n m_1 m_2} \frac{iz}{z^2 + iz\nu(z)} \quad (29)$$

is the correlation function for the transverse components. If the coupling to the non-hydrodynamic subspace is completely ignored, the collision frequency is

$$\nu(z) = i(\Omega^{11} + \Omega^{22}) \quad (30)$$

where

$$\Omega^{\sigma\sigma} = \frac{1}{\rho \sigma k_B T} \int d^3 p d^3 p' p_2 \bar{H}_{\sigma\sigma}(k=0, z | \vec{p}\vec{p}') \phi_\sigma(p') p'_2 \quad (31)$$

In terms of $\nu(z)$ we find

$$D = \frac{c_1 c_2}{S_{cc}} \frac{\rho k_B T}{n m_1 m_2 \nu(0)} \quad (32)$$

Hence, to proceed we need an expression for the memory function.

THE DISCONNECTED APPROXIMATION

The memory function may be expressed in "time space" in the form⁹

$$M_{\sigma\tau}(12;t) = - \sum_{\mu\nu} \int d1' d2' \bar{v}_1 v_{\sigma\mu}(\vec{r}_1 - \vec{r}'_1) \cdot \frac{\partial}{\partial p_1} G_{\sigma\mu; \tau\nu}(11'; 22' | t) \bar{v}_2 v_{\tau\nu}(\vec{r}_2 - \vec{r}'_2) \cdot \frac{\partial}{\partial p_2} \phi_\tau^{-1}(p_2) \quad (33)$$

where the four-point function, $G_{\mu;\nu\tau}$, represents the propagation of pairs of particles between interactions. If this function is simply factored into a product representing the propagation of single particles through the plasma, then in the long time limit M reduces to the usual Lenard-Balescu collision operator.¹⁴ In the Disconnected Approximation the four-point function is factorized in such a way as to preserve its exact initial value. The principal effect of this modified factorization is to renormalize one of the potentials and replace it with a direct

correlation function. An alternative form of this approximation¹⁵ renormalizes both potentials. This has the advantage of giving a positive definite "cross-section", but destroys the short-time behavior of the memory operator. In this paper, the first form of the Disconnected Approximation will be adopted, but some comparisons with the second form will be made.

Using this approximation the collision frequency reduces to

$$\nu(z) = - \frac{1\rho}{3m_1m_2} \int \frac{d^3k}{(2\pi)^3} k^2 \bar{v}_{12}(k) \bar{c}_{12}(k) \int \frac{d\omega_1}{2\pi} \int \frac{d\omega_2}{2\pi} \frac{S_{11}(k, \omega_1) S_{22}(k, \omega_2) - S_{12}(k, \omega_1) S_{21}(k, \omega_2)}{z - \omega_1 - \omega_2} \quad (34)$$

which for low frequencies becomes

$$\nu(0) = - \frac{Z_1 Z_2 e^2 \rho}{3\pi m_1 m_2} \int_0^\infty dk k^2 \bar{c}_{12}(k) \int \frac{d\omega}{2\pi} [S_{11}(k, \omega) S_{22}(k, \omega) - S_{12}^2(k, \omega)] \quad (35)$$

To complete the calculation estimates of the dynamic structure factors are needed. These are obtained by substituting static structure factors obtained from the HNC equation into (23) with $\bar{H}_{\sigma\tau} = 0$.

COMPARISON WITH MOLECULAR DYNAMICS

Calculations of the interdiffusion coefficient have been made using (35) in (32). The results for a 50% mixture of H^+ and He^{2+} at various Γ values are shown in Table I. The reduced diffusion coefficient, D^* , is given by

$$D^* = \left[\frac{S_{cc}}{c_1 c_2} \right] D / r_0^2 \Omega_p \quad (36)$$

Table I. Comparison of theoretical and numerical simulation results for D^* in 50% H^+ - He^{2+} mixture.

Γ	D^*_{MD}	D^*_T	D^*_{GM}
0.4 ^a	3.00	3.18	5.25
1.0 ^b	.915	.792	1.44
4.0 ^a	.142	.154	.265
40. ^a	.0109	----	.0165

^aFrom Ref. 4

^bFrom Ref. 5

Table II. D^* 's for $\text{Si}^{+14}\text{-Sr}^{+36}$ mixtures.

%Si	D^*_{MD}	D^*_T
25	.552	.477
50	.605	.508
75	.628	.545

The subscript MD indicates the results from the Molecular Dynamics studies of Hansen et al.⁴ for $\Gamma = 1$ and Pollock⁵ for $\Gamma = 1$. D^*_T is calculated using the theory described here and D^*_{GM} is calculated from the symmetric form of the Disconnected Approximation.¹⁵ As can be seen from the table, the agreement between D^*_T and D^*_{MD} is quite good for the lower three Γ values. At $\Gamma = 40$, the oscillations in $\epsilon_{12}(k)$ lead to a negative result for D^*_T . The symmetric theory does not run into this difficulty, but it gives results for all Γ values which are 50% too high.

Table II compares the results from the asymmetric theory to computer simulations for mixtures of Si^{+14} and Sr^{+36} at various concentrations, but all at $\Gamma = .005$. Once again the agreement is in the 10-20% range.

TIME CORRELATION FUNCTIONS

In order to study the behavior of the time-correlation function, $V_D(t)$, the high-frequency behavior of $\nu(z)$ is observed to be

$$\nu(z \rightarrow \infty) \rightarrow \frac{i}{z} \frac{4\pi Z_1 Z_2 e^2 \rho}{3m_1 m_2} \quad (37)$$

Using this result in (28) and (29) yields

$$\bar{V}_2(z) = \frac{\rho k_B T}{nm_1 m_2} \frac{i}{z} \left[1 + \left(\frac{i}{z}\right)^2 \left(\Omega_p^2 - \omega_p^2 - \frac{4\pi Z_1 Z_2 e^2 \rho}{3m_1 m_2} \right) + \dots \right] \quad (38)$$

and

$$\bar{V}_1(z) = \frac{\rho k_B T}{nm_1 m_2} \frac{i}{z} \left[1 - \left(\frac{i}{z}\right)^2 \frac{4\pi Z_1 Z_2 e^2 \rho}{3m_1 m_2} + \dots \right] \quad (39)$$

Hence, one notes that

$$\bar{V}_2(t=0)/V_2(t=0) = - \left(\omega_p^2 - \Omega_p^2 + \frac{4\pi Z_1 Z_2 e^2 \rho}{3m_1 m_2} \right) \quad (40)$$

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$$\tilde{V}_L(t=0)/V_L(t=0) = - \frac{4\pi Z_1 Z_2 e^2 p}{3m_1 m_2} \quad (41)$$

Since $\omega_p^2 \geq \Omega_p^2$, the correlations of the longitudinal component of the diffusion velocity have a more rapid initial decay than the transverse components. Combining (40) and (41) gives the known result⁴

$$\tilde{V}_D(t=0)/V_D(t=0) = - \frac{\Omega_p^2}{3} \frac{c_1 m_1^2 Z_2^2 + c_2 m_2^2 Z_1^2}{c_1 Z_1 + c_2 Z_2} \quad (42)$$

The more rapid initial decay of $V_p(t)$ illustrated by the "dashed" and "dash-dot" curves in Figure 1. The solid curve and the dots compare the theoretical estimate of $V_D(t)/V_D(t=0)$ to the corresponding simulation results for the 50% H⁺-He²⁺ mixture at $\Gamma=1$. The comparison is reasonable out to about six inverse plasma frequencies, but the theoretical curve seems to miss the "shoulder" at $12 \omega_p^{-1}$. This may be due to V_p oscillating too rapidly in this region.

DISCUSSION

The results presented here indicate that the Wallenborn and Baus form of the Disconnected Approximation⁴ agrees to about 10-20% with numerical simulation values for the interdiffusion coefficient. Such agreement is quite good, especially in view of the 10% uncertainties in the molecular dynamics results.^{4,5} The only problem arises at very strong coupling where the theory apparently breaks down and gives a negative result. This is not a serious limitation, however, since most plasmas of practical interest are in the weak to moderate coupling regime. In general this calculation is another indication of the success of the Disconnected Approximation.

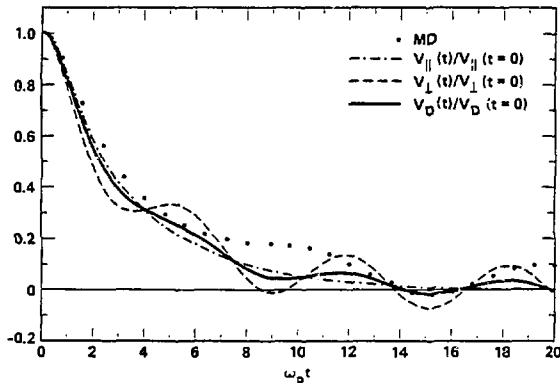


Fig. 1 Normalized velocity autocorrelation functions for 50% H⁺-He²⁺ mixture with $\Gamma = 1$.

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