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Interdiffusion in binary ionic mixtures

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In this paper we present molecular-dynamics and kinetic-theory calculations of the interdiffusion coefficients in dense binary ionic mixtures for conditions appropriate to both astrophysical and inertial-confinement fusion (ICF) plasmas. The diffusion coefficient is the product of a Green-Kubo integral and a thermodynamic prefactor. The molecular-dynamics and kinetic-theory estimates of the Green-Kubo portion agree very well, and it is found that this integral may also be well represented by the usual concentration-weighted sum of self-diffusion coefficients. In addition, the low-density limit of the thermodynamic prefactor is shown to represent an enhancement of the diffusion by the "ambipolar" electric field.

I. 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 multilayer x-ray mirrors should be affected by diffusion, and the evaporation rate of metal "chunks" injected into the fuel of an inertial-confinement fusion (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 formula[2] 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 logarithm[3] can eliminate such unphysical results, but they are untested under these conditions.

In order to gain better understanding of diffusion in dense plasmas we will study a simple model system called a binary ionic mixture (BIM), which consists of 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 $\rho = \rho_1 + \rho_2$. 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

$$\omega_p^2 \equiv \omega_1^2 + \omega_2^2 = \frac{4\pi n_1 Z_1^2 e^2}{m_1} + \frac{4\pi n_2 Z_2^2 e^2}{m_2} = 4\pi n e^2 \overline{Z^2/m} . \tag{1.1}$$

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

$$\Omega_p^2 = 4\pi n e^2 \bar{Z}^2 / \bar{m} \le \omega_p^2 . \tag{1.2}$$

In the above, barred quantities are number weighted averages,

$$\bar{A} = c_1 A_1 + c_2 A_2 , \tag{1.3}$$

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

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 $\mathbf{u}$ is defined by

$$\mathbf{u}(\mathbf{r},t) = \sum_{\sigma=1}^{2} X_\sigma(\mathbf{r},t) \mathbf{u}_\sigma(\mathbf{r},t) , \tag{1.4}$$

where $\mathbf{u}_\sigma$ is the velocity field of species σ, then the mass flux of σ is

$$\mathbf{j}_\sigma(r,t) \equiv \rho_\sigma(\mathbf{r},t)[\mathbf{u}_\sigma(\mathbf{r},t) - \mathbf{u}(\mathbf{r},t)] , \tag{1.5}$$

and the interdiffusion coefficient is defined by the relationship,[4]

$$\mathbf{j}_\sigma(\mathbf{r},t) = -\rho(\mathbf{r},t) D \nabla X_\sigma(\mathbf{r},t) . \tag{1.6}$$

The purpose of this paper is to evaluate D for strongly coupled binary mixtures using both numerical and theoretical methods. Molecular dynamics studies of H^+-He^{2+} mixtures have already been made by Hansen, Joly, and McDonald.[5] The present authors have previously looked at both H^+-He^{2+} and Si^{14+}-Sr^{36+} mixtures.[6] In this paper we report additional simulation results for He^{2+}-C^{6+} mixtures in regions appropriate to the "carbon pollution" problem in white dwarf stars.[7] We also describe a kinetic theory calculation based upon the disconnected approximation[8,9] which gives excellent agreement with all of the simulation results in the regions of greatest interest.

In the next section we will introduce the Green-Kubo expression which relates the diffusion coefficient to the product of an integrated correlation function and a thermodynamic factor. In Sec. III we demonstrate that, at least in the weak-coupling limit, the thermodynamic factor may be thought of as an enhancement of the diffusion due to the "ambipolar" electric field. Our molecular dynamics procedures and results are discussed in Sec. IV, and in Sec. V we present our kinetic theory calculations. Our results are summarized in Sec. VI.

II. GREEN-KUBO RELATION FOR THE DIFFUSION CONSTANT

The diffusion constant, like other transport coefficients, can be expressed in terms of fluctuations in the system in equilibrium, without any external forces to drive a particular mass or energy flux. Derivations of this are available in the literature[10,11] but for completeness we include a simplified derivation which gives the correct result. We consider low-frequency, long-wavelength fluctuations which is the regime governed by linear hydrodynamics. Since we are only interested in diffusion, we consider only mass concentration fluctuations and ignore temperature and pressure fluctuations. Thus only number, and not momentum or energy conservation, must be considered.

The conservation law for, say, species one,

$$\frac{\partial \rho_1(r,t)}{\partial t}+\nabla\cdot\rho_1(r,t)\mathbf{u}_1(r,t)=0\ , \tag{2.1}$$

may be rewritten using the definitions of Sec. I and overall mass conservation as

$$\rho(r,t)\left[\frac{\partial X_1(r,t)}{\partial t}+\mathbf{u}(r,t)\cdot\nabla X_1(r,t)\right]=-\nabla\cdot\mathbf{j}_1(r,t)\ . \tag{2.2}$$

Linearizing this equation and introducing the diffusion constant gives the diffusion equation for mass fluctuations

$$\frac{\partial}{\partial t}\delta X_1(r,t)=D\nabla^2\delta X_1(r,t)\ , \tag{2.3}$$

where $\delta X_1(r,t)$ is the deviation of the mass concentration from its equilibrium value. The free space solution of this equation, in terms of Fourier components is

$$\delta X_1(k,t)=\delta X_1(k,0)e^{-Dk^2t}\ . \tag{2.4}$$

If the initial fluctuation, $\delta X_1(k,\ t=0)$, is assumed to be an equilibrium fluctuation, then averaging over these initial fluctuations and Laplace transforming gives

$$\begin{aligned}\langle\delta X_1(-k,\omega)\delta X_1(k,\ t=0)\rangle &\equiv \int_0^\infty e^{i\omega t}\langle\delta X_1(-k,t)\delta X_1(k,\ t=0)\rangle dt\\ &=\langle\ |\delta X_1(k,\ t=0)|^2\rangle\frac{i\omega+Dk^2}{\omega^2+D^2k^4}\ ,\end{aligned} \tag{2.5}$$

where the angular brackets $\langle\ \rangle$ denote an equilibrium ensemble average. By taking the appropriate limits in this last equation and performing a few manipulations, we obtain a relation for D

$$D=\frac{c_1c_2}{S_{cc}(k=0)}\int_0^\infty dt\ V_D(t)\ , \tag{2.6}$$

where

$$V_D(t)\equiv\frac{1}{3Nc_1c_2}\langle\mathbf{v}_d(t)\cdot\mathbf{v}_d(0)\rangle \tag{2.7}$$

is the autocorrelation function for the (microscopic) diffusion velocity

$$\mathbf{v}_d(t)\equiv c_2\sum_{i\in 1}\mathbf{v}_i(t)-c_1\sum_{i\in 2}\mathbf{v}_i(t)\ . \tag{2.8}$$

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

$$\begin{aligned}S_{cc}(k)&\equiv c_1c_2[c_2S_{11}(k)+c_1S_{22}(k)-2\sqrt{c_1c_2}S_{12}(k)]\\ &=\frac{1}{N}(\rho^2/m_1m_2n)^2\langle\ |\delta X_1(k,\ t=0)|^2\rangle\ .\end{aligned} \tag{2.9}$$

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

$$S_{cc}(k=0)=Nk_BT\Big/\frac{\partial^2G}{\partial c_1^2}\ . \tag{2.10}$$

The presence of the factor $c_1c_2/S_{cc}(k=0)$ stems from our definition of D in terms of the mass concentration gradient rather than the gradient of the chemical potential as is sometime done. For neutral gases, this factor reduces to unity for all concentrations in the low-density limit. For charged particles, however, c_1c_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

$$c_1c_2/S_{cc}(k=0)\to\overline{Z^2}/\bar{Z}^2 \tag{2.11}$$

which is greater than unity whenever $c_1c_2\neq 0$.

We also point out that if the velocity correlations between different particles are neglected, D can be related to the self-diffusion coefficients for the individual species. Specifically, we obtain[4,5]

$$\frac{S_{cc}(k=0)}{c_1c_2}D=c_2D_1+c_1D_2\ , \tag{2.12}$$

where

$$D_\sigma=\int_0^\infty dt\,Z_\sigma(t)\ , \tag{2.13}$$

and

$$Z_\sigma(t)=\tfrac{1}{3}\langle\mathbf{v}_\sigma\cdot\mathbf{v}_\sigma(t)\rangle \tag{2.14}$$

is the velocity autocorrelation function for species σ. This relation is exact in the low-concentration limit, and if

$V_D(t)$ is expanded in powers of t^2 the cross correlations first enter at order t^4.

III. 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 electric field of the electron background is taken into account.

If temperature gradients are neglected, the standard Boltzmann approach gives[12]

$$\mathbf{j}_1 = -\frac{m_1 m_2 n^2}{\rho} D_0 \mathbf{d}_1 , \tag{3.1}$$

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

$$\mathbf{d}_1 = \frac{1}{n}\left[\nabla n_1 - \frac{Z_1 n_1 e}{k_B T}\mathbf{E}\right] + \frac{X_1}{p}\left[\sum_{\sigma=1}^{2} Z_\sigma n_\sigma e \mathbf{E} - \nabla p\right] . \tag{3.2}$$

The ambipolar field is $\mathbf{E}$, and the pressure is given by $p = n k_B T$. If the system is to be mechanically stable, then the sum of the forces on the ions must be balanced by a pressure gradient,

$$\nabla p = (Z_1 n_1 + Z_2 n_2) e \mathbf{E} . \tag{3.3}$$

Requiring charge neutrality over hydrodynamic scale lengths yields

$$Z_1 \nabla n_1 = -Z_2 \nabla n_2 . \tag{3.4}$$

By combining Eqs. (3.1)–(3.4), it is straightforward to obtain

$$\mathbf{j}_1 = -\rho \frac{\overline{Z^2}}{\bar{Z}^2} D_0 \nabla X_1 . \tag{3.5}$$

Comparison with Eq. (2.11) 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.

IV. REMARKS ON MOLECULAR-DYNAMICS SIMULATIONS

The self and interdiffusion constants have been evaluated by molecular dynamics for a model of classical point ions in a uniform, charge neutralizing background. These techniques are by now routine, but there is a question about the ensemble dependence of the computed time correlation function. The molecular-dynamics simulations use a system from a microcanonical ensemble with constant energy, particle number, volume, and total momentum, P. On the other hand, the theoretical results have assumed a canonical or grand canonical ensemble. The differences between averages calculated in these ensembles and by molecular dynamics is due to the presence or absence of energy and momentum fluctuations. For example, the average square of the total momentum is zero in the molecular-dynamics simulations but equal to $3k_B TM$ for a canonical ensemble. Similarly, the energy fluctuations, which are zero in a molecular dynamics simulation, are proportional to the specific heat in a canonical ensemble.

We are interested in the ensemble dependence of $\langle \mathbf{v}_d(t) \cdot \mathbf{v}_d(0) \rangle$. The key point is that the average diffusion velocity is zero in the molecular dynamics experiment. This is still true even if the total momentum were nonzero since adding a drift velocity to all the velocities does not affect $\mathbf{v}_d$. We also need a standard result in statistical mechanics that the ensemble dependence in the correlations of any two dynamical variables A and B is given by[13]

$$\begin{aligned}\langle \delta A \, \delta B \rangle_{\text{ce}} = {} & \langle \delta A \, \delta B \rangle_{\text{MD}} \\ & + \langle (E-\bar{E})^2 \rangle_{\text{ce}} \left[\frac{\partial \langle A \rangle_{\text{MD}}}{\partial E}\right]\left[\frac{\partial \langle B \rangle_{\text{MD}}}{\partial E}\right] \\ & + \langle P^2 \rangle_{\text{ce}} \left[\frac{\partial \langle A \rangle_{\text{MD}}}{\partial P}\right]\left[\frac{\partial \langle B \rangle_{\text{MD}}}{\partial P}\right] \\ & + O(1/N) ,\end{aligned} \tag{4.1}$$

where $\langle \; \rangle_{\text{ce}}$ denotes the canonical ensemble average. Applying this with $A = \mathbf{v}_d(t)$, $B = \mathbf{v}_d(0)$ we see that the ensemble-dependent corrections vanish since $\langle \mathbf{v}_d \rangle_{\text{MD}}$ is zero for all E and P. Therefore, the molecular dynamics correlation function can be used directly in the equations in Sec. II.

V. KINETIC THEORY FOR THE TIME-CORRELATION FUNCTION

A. General theory

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

$$f_\sigma(\mathbf{r},\mathbf{p};t) = \sum_{i \in \sigma} \delta(\mathbf{r}-\mathbf{r}_i(t))\delta(\mathbf{p}-\mathbf{p}_i(t)) . \tag{5.1}$$

If δf_σ represents the deviation of f_σ from its equilibrium average value, then the phase-space correlation functions are

$$C_{\sigma\tau}(\mathbf{r}-\mathbf{r}',t \mid \mathbf{p},\mathbf{p}') \equiv \langle \delta f_\sigma(\mathbf{r},\mathbf{p};t) \delta f_\tau(\mathbf{r}',\mathbf{p}';0) \rangle . \tag{5.2}$$

It is usually more convenient to deal with the transformed functions

$$\tilde{S}_{\sigma\tau}(k,z;\mathbf{p},\mathbf{p}') \equiv \int_0^\infty dt \, e^{izt} \int d^3r \, C_{\sigma\tau}(\mathbf{r}-\mathbf{r}',t \mid \mathbf{p},\mathbf{p}') e^{-i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')} . \tag{5.3}$$

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

$$D=\frac{c_1c_2}{S_{cc}}\mathrm{Re}\widetilde{V}_D(0+i\eta)\quad(\eta\rightarrow 0^+)\ , \tag{5.4}$$

where

$$\widetilde{V}_D(z)=\int_0^\infty dt\, e^{izt}V_D(t)=\tfrac{1}{3}\sum_{\sigma,\tau}\gamma_\sigma\gamma_\tau\int d^3p\int d^3p'\,\widetilde{S}_{\sigma\tau}(k=0,z;\mathbf{p},\mathbf{p}')\mathbf{p}\cdot\mathbf{p}'\ , \tag{5.5}$$

with

$$\gamma_1=\frac{1}{m_1}\left[\frac{c_2}{n_1}\right]^{1/2}\quad\text{and}\quad\gamma_2=\frac{-1}{m_2}\left[\frac{c_1}{n_2}\right]^{1/2}\ .$$

The transformed phase-space correlation functions obey a kinetic equation of the form[14]

$$\left[z-\frac{\mathbf{k}\cdot\mathbf{p}}{m_\sigma}\right]\widetilde{S}_{\sigma\tau}(k,z;p,p')-\sum_{\sigma'}\int d^3\mathbf{p}''\,\Phi_{\sigma\sigma'}(k,z;\mathbf{p},\mathbf{p}'')\widetilde{S}_{\sigma'\tau}(k,z;\mathbf{p}'',\mathbf{p}')=in_\sigma\phi_\sigma(p)[\delta_{\sigma\tau}\delta(\mathbf{p}-\mathbf{p}')+n_\tau\phi_\tau(p')\widetilde{h}_{\sigma\tau}(k)]\ , \tag{5.6}$$

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

$$\widetilde{h}_{\sigma\tau}(k)\equiv\int d^3r\, e^{i\mathbf{k}\cdot\mathbf{r}}[g_{\sigma\tau}(r)-1]\ . \tag{5.7}$$

The operator $\Phi_{\sigma\tau}$ is written as

$$\Phi_{\sigma\tau}(k,z;\mathbf{p},\mathbf{p}')=-n_\sigma\frac{\mathbf{k}\cdot\mathbf{p}}{m_\sigma}\phi_\sigma(p)\widetilde{c}_{\sigma\tau}(k)+\widetilde{M}_{\sigma\tau}(k,z;p,p') \tag{5.8}$$

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

$$\widetilde{c}_{\sigma\tau}(k)=\widetilde{h}_{\sigma\tau}(k)-\sum_{\sigma'}\widetilde{c}_{\sigma\sigma'}(k)\widetilde{h}_{\sigma'\tau}(k) \tag{5.9}$$

and the "memory" function $\widetilde{M}_{\sigma\tau}$ which contains the effects of collisions.

The standard procedure for solving Eq. (5.6) is to expand the momentum dependence of the $\widetilde{S}_{\sigma\tau}$'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,[15] and its complement, the "nonhydrodynamic" subspace. Projecting the kinetic equation onto the "hydrodynamic" subspace then yields a closed set of equations for the hydrodynamic matrix elements of the $\widetilde{S}_{\sigma\tau}$'s. The details of this procedure are well described in the paper by Baus[16] and will not be given here.

Applying Baus' method to the problem at hand ultimately yields

$$\widetilde{V}_D(z)=\tfrac{1}{3}\widetilde{V}_l(z)+\tfrac{2}{3}\widetilde{V}_\perp(z)\ , \tag{5.10}$$

where

$$\widetilde{V}_l(z)=\frac{\rho k_BT}{nm_1m_2}\frac{iz(z^2-\Omega_p^2)}{z^2(z^2-\omega_p^2)+iz\nu(z)(z^2-\Omega_p^2)} \tag{5.11}$$

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

$$\widetilde{V}_\perp(z)=\frac{\rho k_BT}{nm_1m_2}\frac{iz}{z^2+iz\nu(z)} \tag{5.12}$$

is the correlation function for the transverse components. If the coupling to the nonhydrodynamic subspace is completely ignored,[17] the collision frequency is

$$\nu(z)=i(\Omega^{11}+\Omega^{22})\ , \tag{5.13}$$

where

$$\Omega^{\sigma\sigma}=\frac{1}{\rho_\sigma k_BT}\int d^3p\int d^3p'\,p_l\widetilde{M}_{\sigma\sigma}(k=0,z\mid\mathbf{p},\mathbf{p}')\times\phi_\sigma(p')p_l'\ . \tag{5.14}$$

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

$$D=\frac{c_1c_2}{S_{cc}}\frac{\rho k_BT}{nm_1m_2\nu(0)}\ . \tag{5.15}$$

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

B. The disconnected approximation

The memory function may be expressed in "time-space" in the form[14]

$$M_{\sigma\tau}(12;t)=-\sum_{\mu,\nu}\int d1'\int d2'\,\boldsymbol{\nabla}_1v_{\sigma\mu}(\mathbf{r}_1-\mathbf{r}_1')\cdot\frac{\partial}{\partial\mathbf{p}_1}G_{\sigma\mu;\tau\nu}(1,1';2,2'\mid t)\boldsymbol{\nabla}_2v_{\tau\nu}(\mathbf{r}_2-\mathbf{r}_2')\cdot\frac{\partial}{\partial\mathbf{p}_2}\phi_\tau^{-1}(p_2)\ , \tag{5.16}$$

where the four-point function $G_{\sigma\mu;\nu\tau}$ 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.[18] In the disconnected approximation the four-point function is factorized in such a way as to preserve its exact initial value.[9] The principal effect of this

TABLE I. Diffusion coefficients (in $\mathrm{cm}^2/\mathrm{sec}$) for 50% H^+-He^{2+} mixtures with $n = 10^{22}\ \mathrm{cm}^{-3}$ from (a) Ref. 5 and (b) Ref. 6.

	Simulations				Theory				
Γ	D_{H}	D_{He}	D'	$\bar{D}$	D_{H}	D_{He}	D'	$\bar{D}_{\mathrm{WB}}$	$\bar{D}_{\mathrm{GM}}$
0.4 (a)	0.519	0.153	0.336	0.311	0.477	0.145	0.311	0.329	0.544
1.0 (b)	0.122	0.0488	0.0854	0.0946(5)	0.109	0.0418	0.075	0.082	0.149
4.0 (a)	0.0205	0.0109	0.0157	0.0147	0.0198	0.0126	0.0162	0.0159	0.0274
40.0 (a)	0.001 11	0.000 65	0.001 13	0.000 88					0.001 71

modified factorization is to renormalize one of the potentials and replace it with a direct correlation function. An alternative form of this approximation[8] 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

$$\nu(z) = -\frac{i\rho}{3m_1 m_2}\int \frac{d^3k}{(2\pi)^3} k^2 \tilde{v}_{12}(k)\tilde{c}_{12}(k) \int \frac{d\omega_1}{2\pi}\int \frac{d\omega_2}{2\pi} \frac{S_{11}(k,\omega_1)S_{22}(k,\omega_2) - S_{12}(k,\omega_1)S_{21}(k,\omega_2)}{z-\omega_1-\omega_2}\ , \tag{5.17}$$

which for low frequencies becomes

$$\nu(0) = -\frac{Z_1 Z_2 e^2 \rho}{3\pi m_1 m_2}\int_0^\infty dk\, k^2 \tilde{c}_{12}(k) \int \frac{d\omega}{2\pi}[S_{11}(k,\omega)S_{22}(k,\omega) - S_{12}^2(k,\omega)]\ . \tag{5.18}$$

To complete the calculation estimates of the dynamic structure factors are needed. These are obtained by substituting static structure factors obtained from the hypernetted chain (HNC) equation into Eq. (5.6) with $\tilde{M}_{\sigma\tau} = 0$. Applying the same method to Eq. (2.15) yields expressions for the self-diffusion coefficients.

C. 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

$$\nu(z \to \infty) \to \frac{i}{z}\frac{4\pi Z_1 Z_2 e^2 \rho}{3m_1 m_2}\ . \tag{5.19}$$

Using this result in Eqs. (5.11) and (5.12) yields

$$\tilde{V}_l(z) = \frac{\rho k_B T}{n m_1 m_2}\frac{i}{z}\left[1 - \left[\frac{i}{z}\right]^2 \left[\omega_p^2 - \Omega_p^2 + \frac{4\pi Z_1 Z_2 e^2 \rho}{3m_1 m_2}\right] + \cdots\right] \tag{5.20}$$

and

$$\tilde{V}_\perp(z) = \frac{\rho k_B T}{n m_1 m_2}\frac{i}{z}\left[1 - \left[\frac{i}{z}\right]^2 \frac{4\pi Z_1 Z_2 e^2 \rho}{3m_1 m_2} + \cdots\right]\ . \tag{5.21}$$

Hence, one notes that

$$\ddot{V}_l(t=0)/V_l(t=0) = -\left[\omega_p^2 - \Omega_p^2 + \frac{4\pi Z_1 Z_2 e^2 \rho}{3m_1 m_2}\right]\ , \tag{5.22}$$

$$\ddot{V}_\perp(t=0)/V_\perp(t=0) = -\frac{4\pi Z_1 Z_2 e^2 \rho}{3m_1 m_2}\ . \tag{5.23}$$

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 Eqs. (5.22) and (5.23) gives the result

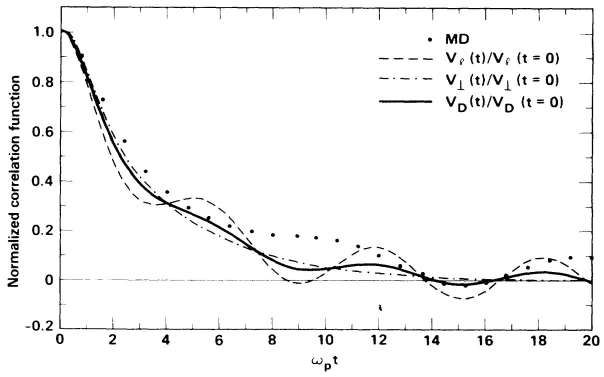

FIG. 1. Normalized velocity correlation functions for 50% H^+-He^{2+} mixture with $\Gamma = 1$.

TABLE II. Diffusion coefficients (in cm^2/sec) for Si^{14+}-Sr^{36+} mixtures with $n=10^{22}$ cm^{-3}, $T=1$ keV ($\Gamma=0.005$).

	Simulations				Theory			
% Si	$D_{\rm Si}$	$D_{\rm Sr}$	D'	$\bar{D}$	$D_{\rm Si}$	$D_{\rm Sr}$	D'	$\bar{D}$
0.1					0.185		0.185	0.185
25.0	0.259	0.088	0.217	0.215(17)	0.215	0.0775	0.181	0.186
50.0	0.325(3)	0.105(1)	0.215	0.217(10)	0.263	0.0904	0.177	0.182
75.0	0.408(4)	0.128(2)	0.197	0.204(15)	0.349	0.113	0.172	0.177
99.9						0.168	0.168	0.168

$$\ddot{V}_D(t=0)/V_D(t=0) = -\frac{\Omega_p^2}{3}\frac{c_1 m_1^2 Z_2 + c_2 m_2^2 Z_1}{(c_1 Z_1 + c_2 Z_2) m_1 m_2} \tag{5.24}$$

The more rapid initial decay of $V_l(t)$ is illustrated by the "dashed" and "dash-dot" curves in Fig. 1. The solid curve is the theoretical estimate of $V_D(t)/V_D(t=0)$ as defined in Eq. (5.10), and the dots are the simulation results for the 50% H$^+$-He^{2+} mixture at $\Gamma=1$. The comparison between the theoretical and molecular dynamics (MD) results is reasonable out to about six inverse plasma frequencies, but the theoretical curve seems to miss the "shoulder" at $12\omega_p^{-1}$.

VI. RESULTS AND DISCUSSION

We have evaluated diffusion coefficients for three pairs of ions. Results for a 50% mixture of H$^+$-He^{2+} at $\Gamma=1$ are shown in Table I along with the results of Hansen *et al.*[5] for the same mixture at a variety of other Γ values. Table II shows results at a fixed Γ for various concentrations of Si^{14+}-Sr^{36+}, while in Table III we show coefficients for He^{2+}-C^{6+} at Γ values and concentrations selected from a model white dwarf atmosphere.[19] The Green-Kubo portion of the interdiffusion coefficient is indicated by $\bar{D}$ and the estimate of $\bar{D}$ based upon Eq. (2.12) is D'. Molecular dynamics results are on the left side of each table; kinetic theoretic results are on the right.

In Table I we show two kinetic theoretic results of $\bar{D}$. One is based upon the "asymmetric" theory $\bar{D}_{\rm WB}$ described in detail here and in Ref. 9. The other, $\bar{D}_{\rm GM}$, is based upon the "symmetric" theory of Ref. 8. As can be seen from the table the agreement between the simulation results and $\bar{D}_{\rm WB}$ is quite good for the lower three Γ values. For $\Gamma=40$ the oscillations in $\tilde{c}_{12}(k)$ lead to a negative value for $\bar{D}_{\rm WB}$. The symmetric theory does not run into this difficulty, but it gives results for all Γ values which are about 50% too high. In the moderate coupling region of greatest practical interest the asymmetric theory is definitely preferred.

In Table II, we compare the asymmetric theory to simulations of Si^{14+}-Sr^{36+} mixtures at $\Gamma=0.005$, with 25%, 50%, and 75% Si^{14+}. Here, and in the other two tables, the agreement between D and D' is at the same level (10%) as the uncertainties in the simulation results for $\bar{D}$. Both the kinetic theory and the simulations show little variation in $\bar{D}$ as the concentration is changed. However, the self-diffusion coefficients do decrease as more Sr^{36+} is added and the plasma becomes more strongly coupled ($\bar{Z}^2\Gamma$ gets larger). As this occurs the interdiffusion is increasingly dominated by the more mobile Si^{14+} ions. As a result the interdiffusion coefficient shows much less variation than the self-diffusion coefficients.

Results for He^{2+}-C^{6+} are shown in Table III. The concentration and the Γ of the mixture were varied simultaneously to reflect values at various depths in a model white dwarf atmosphere. The more strongly coupled cases are deeper in the white dwarf envelope. Once again the agreement between theory and simulation is quite good. We note here that the diffusion model of Paquette *et al.*[1] is also in very good agreement with the MD results.[19]

In general, the results presented here indicate that the Wallenborn and Baus form of the disconnected approximation agrees to about 10–20% with numerical simulation results for diffusion coefficients in binary ionic mixtures. The only problem arises at very strong coupling where the theory breaks down and gives a negative result.

TABLE III. Diffusion coefficients (in cm^2/sec) for He^{2+}-C^{6+} mixtures for conditions in a white dwarf atmosphere.

			Simulations				Theory			
% He	T (keV)	n (10^{26} cm^{-3})	$D_{\rm He}$	$D_{\rm C}$	D'	$\bar{D}$	$D_{\rm He}$	$D_{\rm C}$	D'	$\bar{D}$
20	0.739	0.877	0.0472(6)	0.0117(2)	0.0401	0.038(2)	0.0402	0.0100	0.0342	0.0345
50	1.00	1.50	0.0575(4)	0.0146(2)	0.0361	0.040(2)	0.0522	0.0156	0.0339	0.0327
80	1.49	3.72	0.075(1)	0.0187(5)	0.0300	0.031(3)	0.0707	0.0166	0.0274	0.0274

This does not appear to be a serious limitation, since most plasmas of practical interest are in the weak to moderate coupling regime. Finally, our results corroborate the conclusion[5] that the interdiffusion coefficient can be well approximated by an appropriate average of self-diffusion coefficients.

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