Corresponding States Hard-Sphere Model for the Diffusion Coefficients of Binary Dense-Plasma Mixtures

Yaakov Rosenfeld
Nuclear Research Center Negev, P.O. Box 9001, Beer-Sheva 84190, Israel

Eran Nardi and Zeev Zinamon
Weizmann Institute of Science, Rehovot 76100, Israel
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A recent free-energy model for charged Yukawa mixtures enables one to obtain, in simple analytic form, the diffusion coefficients of dense plasmas from those for "effective" hard spheres. This hard-sphere model was checked by new molecular dynamics simulations of highly asymmetric binary ionic mixtures to demonstrate a corresponding states relation for the diffusion coefficients in terms of the excess entropy. It is accurate for moderately coupled plasmas, as well as for strongly coupled plasmas, when the kinetic theoretic approximation breaks down.

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Ionic diffusion in dense plasma mixtures has been of interest recently [1–8] in many quite disparate fields: (1) Diffusion is central for understanding the distribution of heavy elements in the atmospheres of white dwarf stars, and the composition of fluid planets. (2) It affects the performance of multilayer x-ray mirrors. (3) Interdiffusion coefficients control the evaporation rate of metal injected into the fuel of an inertial-confinement fusion (ICF) capsule by hydrodynamic instabilities [9]. (4) There are many laboratory situations in which it is important to know how fast two hot, ionized materials mix across an initially sharp interface. In all these applications the fluid can be dense, and estimates based on, e.g., the Chapman-Spitzer formulas [10,11] for gases are not adequate despite recent advances [5] which yielded a more systematic treatment of the Coulomb logarithm in the collision integral. The accuracy of approximations based on kinetic theory, which are supposed to extend Chapman and Spitzer to high densities, cannot be judged *a priori,* and these have to be gauged by simulations.

Molecular dynamics (MD) simulations for the interdiffusion coefficient in binary Coulomb plasma mixtures have been performed in recent years for systems with low asymmetry of the charges and of the masses [1–4,6]. These results supplement a large body of data for single component systems with various interparticle potentials [12–14], as well as results for the interdiffusion coefficients in mixtures of noble gases described by the Lennard-Jones potential [15] and in mixtures of hard spheres [16]. Results of equilibrium MD simulations using the Green-Kubo relations and the velocity autocorrelations agree to within a few percent [17] with those obtained from nonequilibrium MD in which a "current" due to some external field is measured. The simulations, and in particular for mixtures, are very time consuming; they suffer from inherent problems related to long time tails, and are estimated to have 10%–20% accuracy at best. A kinetic theoretic approximation to the diffusion coefficients which generalizes Spitzer to high density was described [3,4], which is in good agreement with the computer simulations [1–4] in the weak to moderate coupling regime, but which breaks down in strong coupling.

Many of the simulations for the transport coefficients of strongly coupled one-component fluids can be correlated with equilibrium thermodynamic properties according to the plot of a reduced (dimensionless) coefficient as a function of the reduced excess (i.e., configurational, over ideal-gas value) entropy [18]. The diffusion coefficients can thus be estimated within about 30% by using corresponding states values based on the excess entropy [13,18,19]. Because of the choice of macroscopic reduction parameters (volume and temperature) for the transport coefficient rather than microscopic potential parameters, this corresponding states relation [18] can be and has been applied directly to real materials [19]. The excess-entropy corresponding states were motivated [18] by the success of the (variational) hard-sphere (HS) perturbation theory [20] for simple fluids in which the hard-sphere radius, or equivalently the excess entropy, was used to parametrize the structure of equilibrium fluids.

This Letter extends the excess-entropy corresponding states to moderately and strongly coupled plasma mixtures. A recent comprehensive and accurate free-energy model [21] for charged Yukawa mixtures enables one to obtain, in simple analytic form, the diffusion coefficients of dense plasmas from those for "effective" hard spheres. Using a standard code [22] modified to treat Ewald potentials for Yukawa charges (see Ref. 34 in [21]), the results of this hard-sphere model were checked by new molecular dynamics simulations of binary ionic mixtures, with high asymmetry in the charges and masses, to demonstrate a corresponding states relation for the diffusion coefficients in terms of the excess entropy.

Many quite disparate systems with screened Coulomb interactions, including dense stellar materials and inertially confined plasmas, can be described by Yukawa interparti-

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cle potentials, $e - \alpha r/r$, which make important reference systems in condensed matter physics [23]. We consider classical binary mixtures ($i = 1, 2$), consisting of N_i positively charged $Z_i e > 0$, $Z_2 \geq Z_1$, point particles of mass M_i, interacting through the Yukawa pair potentials

$$u_{ij}(r)/k_B T = Z_i Z_j \Gamma e^{-\alpha r}/r. \quad (1)$$

Measuring distances in units of the total Wigner-Seitz radius, $a = (3/4\pi n)^{1/3}$, $n = N/V \equiv (N_1 + N_2)/V$ is the total number density, $\Gamma = e^2/ak_B T$ is the conventional plasma coupling parameter, and T is the temperature. We estimate the diffusion coefficients for the Yukawa particles by those for the "effective" hard spheres. We thus need the "effective" hard-sphere radii R_1, R_2 for the charged Yukawa particles or, alternatively, the ratio $\xi = R_2/R_1 \geq 1$ and the total packing fraction η of these effective spheres.

For a one-component Yukawa system with $Z_i = 1$, the configurational (excess) entropy, in units of Nk_B, is a function of two variables: $s \equiv S^{\text{conf}}/Nk_B = s(\Gamma, \alpha)$. For the mixture, it depends also on the charges and on the relative concentrations, $x \equiv x_2 = N_2/N = 1 - x_1$, $S^{\text{conf}}_{\text{mix}}/Nk_B = s_{\text{mix}}(x, Z_1, Z_2, \Gamma, \alpha)$. The approximate scaling law for Yukawa mixtures has the form [21]

$$s_{\text{mix}} = (1 - x)s(\Gamma_1, \alpha_1) + xs(\Gamma_2, \alpha_2), \quad (2)$$

where ($i = 1, 2$)

$$\Gamma_i = (Z_i^2/\lambda_i)\Gamma, \qquad \alpha_i = \alpha\lambda_i, \quad (3)$$

and where the λ_i are obtained from the solution of the following set of nonlinear coupled algebraic equations:

$$\lambda_i^3 = \frac{Z_i Q(\alpha\lambda_i)}{(1 - x)Z_1 Q(\alpha\lambda_1) + xZ_2 Q(\alpha\lambda_2)}, \quad i = 1, 2. \quad (4)$$

The plasma is weakly, moderately, or strongly coupled according to whether $\Gamma_{\text{eff}} = x_1\Gamma_1 + x_2\Gamma_2 \ll 1$, ~ 1, or $\gg 1$, respectively. The function $Q(t) = 2t^3/3[e^t(t - 1) + e^{-t}(t + 1)] \leq 1$ has the following physical meaning: The Yukawa intermolecular potential has the special property [21] that the potential outside a spherically symmetric uniform distribution of charge Z_i, inside a sphere of radius λ_i, retains the Yukawa form, but the charge is renormalized by the factor $1/Q(\alpha\lambda_i)$, i.e., $\Phi(r \geq \lambda_i) = [Z_i/Q(\alpha\lambda_i)]/e^{-\alpha r}/r$. The Gauss-Newton theorem for the Coulomb potential ($\alpha = 0$) is manifestly satisfied by $Q(0) = 1$, $\lambda_i = (Z_i/\langle Z\rangle)^{1/3}$, and the Yukawa mixing rule [21] corresponds to the "linear mixing rule" [24] approximation for unscreened plasmas. The Yukawa mixing rule has a simple physical meaning in the context of the Thomas-Fermi model for the equation of state of mixtures of elements [21].

The λ_i play the role of effective hard-sphere radii. They also correspond [21] to the asypmtotic strong coupling limit of the variational hard-sphere model using the Percus-Yevick approximation for which the ratio ξ does not vary strongly with the coupling parameter Γ. We thus maintain a fixed ratio of the hard-sphere radii

$$\xi = \lambda_2/\lambda_1. \quad (5)$$

The relatively high accuracy fo the Percus-Yevick (PY) theory [25] for the pair correlation functions and equation of state of hard-sphere mixtures, except for very special conditions corresponding to phase separation (which is not predicted by the PY theory), have been demonstrated once again by recent density functional calculations [26]. Using the "compressibility" PY excess entropy of the hard-sphere mixture $s_{\text{mix,HS}}$, we use Eqs. (2)–(5) and solve the following equation to obtain η:

$$s_{\text{mix,HS}}(\eta, \xi, x) = s_{\text{mix}}(\Gamma_1, \alpha_1, \Gamma_2, \alpha_2, x). \quad (6)$$

An accurate estimate of the excess entropy for the one-component Yukawa system $s(\Gamma, \alpha)$ is obtained by using the variational fitting procedure [27]: Apply the variational hard-sphere model with the PY pair functions to the one-component Yukawa and adjust the hard-sphere excess entropy function $s_{\text{HS}}(\eta) = s_{\text{mix,HS}}(\eta, \xi = 1, x) + \Delta s(\eta)$, with $\Delta s(\eta)$ chosen to fit the simulation results [28] for the unscreened Coulomb potential.

For the diffusion coefficients we use the Chapman-Enskog approximation for hard-sphere mixtures as given by Chapman and Cowling (pp. 165 and 170 in Ref. [11]) and by Ref. [29], corrected in view of new simulation results [16]. It is essentially the dilute gas result for hard spheres rescaled by the pair contact probability. For plasmas it is customary to present the reduced coefficients $D^* = D/\omega_p a^2$, where ω_p is the plasma frequency $\omega_p = (4\pi n e^2\langle Z^2\rangle/\langle M\rangle)^{1/2}$, while $\langle M\rangle = (1 - x)M_1 + xM_2$ and $\langle Z_2\rangle = (1 - x)Z_1^2 + xZ_2^2$ denote weighted averages. The results are given by

$$D_j^* = \frac{D_j}{\omega_p a^2} = \frac{(\langle M\rangle/M_j)^{1/2} C}{8(\frac{3}{\pi})^{1/2}\eta_1^{2/3}(\Gamma\langle Z^2\rangle)^{1/2} W_j}, \quad (7)$$

where the index j corresponds to one of the three cases $j = 1, 2, 12$. The two self-diffusion coefficients are D_1, D_2, the interdiffusion coefficient is D_{12}, $M_{12} = 2M_1M_2/(M_1 + M_2)$, $\eta_1 = \eta/[1 + x(\xi^3 - 1)]$, and

$$W_1 = (1 - x)G_{11} + \frac{x}{4}G_{12}(1 + \xi)^2(\langle M_{12}\rangle/M_1)^{1/2},$$

$$W_2 = xG_{22}\xi^2 + \frac{1 - x}{4}G_{12}(1 + \xi)^2(\langle M_{12}\rangle/M_1)^{1/2}, \quad (8)$$

$$W_{12} = \frac{1}{4}G_{12}(1 + \xi)^2,$$

where $G_{ij} = g_{ij}(r = R_i + r_j)$ are the contact values [25] of the Percus-Yevick radial distribution functions $g_{ij}(r)$. C is an optional correcton factor of about unity which we choose here as $C = C_1(\eta)C_2(s_{\text{mix}})$. $C_1(\eta)$ is the ratio (~ 1) between the simulation and Chapman-Enskog values for the diffusion coefficient for the one-component hard spheres [16]. $C_2(s_{\text{mix}})$ is the factor (~ 1) which adjusts (to about 20%) the present hard-sphere

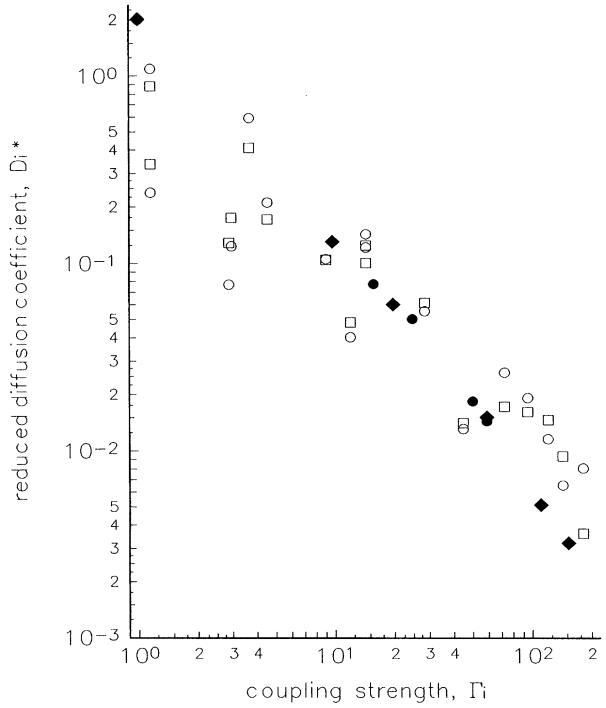

FIG. 1. Reduced diffusion coefficient $D_i^*(i = 1, 2)$ as a function of the coupling parameter Γ_i. The filled diamonds (Ref. [14]) and circles (present) are the MD results for the one-component Coulomb plasma (OCP) to which the present model is adjusted by the factor $C \sim 1$. The open squares are the present MD results for equimolar ($x = 0.5$) binary Coulomb plasma mixtures, while the open circles are the corresponding results of the hard-sphere model; every Γ_i entry in Table I is represented by a pair of one open circle and one open square.

model to the simulation results for the one-component Coulomb plasma [14] (see Fig. 1). Setting $C = 1$ does not change the overall picture obtained from the hard-sphere model.

The MD runs used 216 particles, and the self-diffusion coefficients were calculated from intergals of the velocity autocorrelation functions and from the mean square displacement of the particles, with good agreement between these two estimates. The interdiffusion coefficient

TABLE I. Reduced diffusion coefficients for equimolar binary Coulomb-plasma mixtures (see Fig. 1). Present MD results (D^*) compared with the hard-sphere model ($\overline{D^*}$).

M_2/M_1	Z_2/Z_1	Γ_1	D_1^*	$\overline{D_1^*}$	Γ_2	D_2^*	$\overline{D_2^*}$
4	2	1.15	0.88	1.09	3.66	0.41	0.59
4	2	4.54	0.17	0.21	14.4	0.10	0.12
4	2	9	0.104	0.105	28.5	0.061	0.055
4	2	44.9	0.014	0.013	143	0.0066	0.0065
10	4	11.97	0.048	0.040	120.7	0.0145	0.0115
25	8	2.97	0.174	0.123	95.1	0.016	0.019
40	12	0.23	5.1	1.2	14.4	0.124	0.142
40	12	1.15	0.336	0.237	72.5	0.017	0.026
40	12	2.88	0.128	0.077	181	0.004	0.008

TABLE II. Reduced diffusion coefficients for the H/He mixture ($M_2/M_1 = 4$, $Z_2/Z_1 = 2$). MD results D_{12}^* from Ref. [2] and present D_1^*, D_2^*, compared with the hard-sphere model ($\overline{D_1^*}$, $\overline{D_1^*}$, $\overline{D_{12}^*}$).

x	Γ	D_1^*	$\overline{D_1^*}$	D_2^*	$\overline{D_2^*}$	D_{12}^*	$\overline{D_{12}^*}$
0.50	39.74	0.0113	0.0123	0.0066	0.0063	0.0109	0.0097
0.75	40.83	0.0168	0.0165	0.0107	0.0090	0.0122	0.0114
0.25	40.61	0.0073	0.0079	0.0040	0.0039	0.0076	0.0071

is a product of a Green-Kubo intergral and a thermodynamic prefactor which can be well approximated by unity in the moderate and strong coupling regimes. We obtained very good agreement with the literature data for the one-component plasms (OCP) [14] and for the H/ He mixture [1–4], and we estimate the accuracy of our results for the diffusion coefficients to be about 20%.

The MD results are compared with the hard-sphere model in Fig. 1 and in Tables I–IV. We considered a wide range of values for the mass, M_2/M_1, and charge, Z_2/Z_1, ratios. For unscreened (Coulomb) plasmas the following general picture emerges: (1) The thermodynamic scaling parameters Γ_i are also relevant for understanding the results for the diffusion coefficients. (2) As long as $\Gamma_i \gtrsim 1$, when i denotes any one of the plasma components, the hard-sphere model results for the diffusion coefficient D_i^* of the same component is accurate to about 30% for results with variations of three orders of magnitude. (3) It has been previously demonstrated [1–4] that the interdiffusion coefficient, D_{12}, can be well represented by an appropriate average, D_{12}', of self-diffusion coefficients, $D_{12} \approx D_{12}' = I_T[x_2 D_1 + x_1 D_2]$. For moderately and strongly coupled plasmas the thermodynamic factor I_T can be replaced by unity $I_T = 1$. Our MD results extend the validity of this approximation also for highly asymmetric mixtures. In agreement with Ref. [2] we find that D_{12}' is somewhat smaller than D_{12}, but the difference does not exceed 20%. (4) Moreover, the predictions of the hard-sphere model of the ratio D_{12}/D_{12}' are accurate to better than 10%. For example, for the cases in rows 1, 2, 4, 8, and 9 in Table I, the MD results are $D_{12}/D_{12}' = 1.12$, 1.00, 1.02, 1.20, 1.14, and the hard-sphere model results are $D_{12}/D_{12}' = 1.05$, 1.05, 1.05, 1.12, 1.12, respectively.

This picture remains true also for screened plasmas, but with somewhat less agreement between the MD results and the hard-sphere model. The screening reduces the

TABLE III. Reduced interdiffusion coefficient for the Si^{14+}-Sr^{36+} mixture ($M_2/M_1 = 88/28$) at $\Gamma = 0.005$ (i.e., $\Gamma_1 \sim 1$, $\Gamma_2 \sim 6$). MD results (D^*) from Refs. [1,3] compared with the hard-sphere model ($\overline{D^*}$).

x	D_1^*	$\overline{D_1^*}$	D_2^*	$\overline{D_2^*}$	D_{12}^*	$\overline{D_{12}^*}$
0.75	0.665	0.515	0.226	0.265	0.552	0.459
0.50	0.906	0.676	0.293	0.357	0.605	0.530
0.25	1.256	0.996	0.394	0.545	0.628	0.676

TABLE IV. Screening effects on the diffusion coefficients for the equimolar H/He mixture. Ratio $\Lambda_i = D_i/D_i^{(\alpha=0)}$ as a function of α for two values of Γ. Present MD results (Λ) compared with the hard-sphere model ($\overline{\Lambda}$).

Γ	α	Λ_1	$\overline{\Lambda_1}$	Λ_2	$\overline{\Lambda_2}$
4	1.03	1.09	1.60	1.23	1.63
4	2.06	1.73	2.90	1.71	3.10
40	1.03	1.37	1.85	1.44	1.89
40	2.06	2.48	3.90	2.87	4.19

effective radius of the charges and increases the diffusion coefficients (Table IV). There is one MD data point in the literature [8] for the one-component Yukawa potential: $\Gamma = 50$, $\alpha = 2.17$, $D^* = 0.042$ (vs $D^* = 0.015$ for $\alpha = 0$). Our MD results are $D^* = 0.040$ (vs $D^* = 0.018$), and our hard-sphere model results are $D^* = 0.065$ (vs $D^* = 0.018$), respectively. Small adjustments of the one-component fitting function [see after Eq. (6)] $\Delta s(\eta)$ can improve the hard-sphere model to 20% accuracy also for screened mixtures. Additional improvement in accuracy for both Coulomb and Yukawa plasmas can be gained by relaxing the constraint (5) and by allowing the ratio of radii ξ to vary with Γ (e.g., according to the full solution of the variational hard-sphere model).

From these comparisons of the hard-sphere model with the MD simulations, there emerges a physical picture of the moderately and strongly coupled plasma in which the contribution of each component is weakly dependent of the other, such as the confined Thomas-Fermi atoms for determining the equation of state. These Thomas-Fermi atoms behave as if they were hard spheres. The hard-sphere model keeps up the accuracy of the successful kinetic theoretic approximations in the moderate coupling regime, yet it retains high accuracy also in the strong coupling regime where the kinetic theory breaks down. In addition to providing the first accurate model which extends the Spitzer theory all the way to strongly coupled plasmas, the corresponding states hard-sphere model is useful in making estimates of unknown constitutive properties nad for suggesting theoretical analyses of regularities found empirically.

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