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The Interaction of Debye-Shielded Particles

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The Interaction of Debye-Shielded Particles

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Abstract

Macroscopic particles or solid surfaces in contact with a typical low-temperature plasma immediately charge negatively and surround themselves with an electron-depleted region of positive charge. This Debye shielding effect is involved in the Debye-Hückel theory in liquids and plasma sheath formation in the gas phase. In this report, the interaction between such screened particles is found by using the same basic approximation that is used in constructing the Debye shielding potential itself. The results demonstrate that a significant attraction exists between the particles, and, if conditions are right, this attractive force can contribute to the generation of particulate plasma crystals.

I. Introduction

In 1986 Ikezi¹ predicted the existence of crystals of particulates (particles) in a plasma environment. Since then there have been several observations of such crystals^{2 3 4 5 6 7 8 9 10 11} as well as theoretical studies related to the crystallization.^{12 13 14}

There is a general feeling that the observations support some kind of weak attraction between the screened particles, but the mechanism for the formation of an attractive force is not known for certain. The arguments for an attractive force have been based on some features of the observations as well as computer simulations of the plasma in the neighborhood of the particles.^{15 16} Although these simulations are the best fundamental approach to the complex problem, no general form of the interaction has been predicted.

In this report the formation of the Debye-shielded particle is analyzed from a classic point of view and the predictions for a system of several particles in a plasma background are made from the same analysis. The results are interesting and predict the existence of a weak binding potential between the particles. Whether or not this interaction is strong enough to contribute to the plasma particle crystallization depends on thermal conditions within the plasma.

In general the previous investigators have favored dipole-dipole interactions which can be generated in the plasma crystals due to the spatial anisotropy of the plasma environment. These dipole-dipole interactions, as well as other forms of interaction due to the steady-state dynamics, may be stronger than the interaction that will be discussed here. A study of the relative strengths will be performed later. The purpose of this report is to present the Debye-shielded interaction model.

II. Debye Shielding in a Plasma Environment

What will be done here is to take the assumptions that go into the solution of the Debye sheath surrounding a particle in a plasma and generalize it to several particles. In so doing, one sees that the theory predicts a net attraction of the particles at long range. This is not surprising, since the system bears analogy to the interaction of two atoms with their associated charge distributions.

Consider a solid body (the particle) in contact with a plasma. The electrons will be assumed to be at a nominal temperature of a few eV. The ions will be typically colder, and, in any case, always moving considerably slower than the electrons. The nearly equal ion and electron densities and the disparate velocities, combined with high probabilities of sticking at the particle surface, create a selective negative charging of the particle. Ions and electrons that encounter the solid body will

be assumed to stick with near unit accommodation. The ions may in fact react and leave the surface as neutrals. However this counts as removal as charged species, so we simply view the process as near unit accommodation of ions and electrons. This kinetic aspect of the collisions with the solid creates the plasma sheath,¹⁷ with a net negative charge accumulating on the body. This accumulation of charge retards the flow of electrons to the body and accelerates the flow of ions. The charge will stabilize when the fluxes to the body are equal (or nearly so regarding the near equal electron and ion sticking coefficients). The first aspect of the Debye problem is to calculate the charged particle fluxes and the amount of charging of the body.

For the electrons, one assumes a Boltzmann distribution within the potential field that exists throughout the plasma. This potential is the time-averaged quantity (regarding the heavy particles as fixed) and not the instantaneous field of all the charges in the system. The field will be symbolized as $\phi(\vec{r})$. Thus one has the usual distribution of number density of the electrons in the plasma:

$$n_e(\vec{r}) = n_\infty \exp\left(\frac{e\phi(\vec{r})}{k T_e}\right). \quad (1)$$

The quantity n_∞ refers to the electron (plasma) density far from the particle where the reference setting of the potential is zero. Eq.(1) predicts that the electron density decreases near the particle where the potential is negative. The ion density also varies in the vicinity of the particle. However it is not so easy to estimate the ion distribution.¹⁸ First of all, there can be a neutral gas background within the plasma which helps the transition to equilibrium conditions. If the ions are truly thermalized or canonical, their density peaks near the particle as seen from the ion Boltzmann distribution:

$$n_i(\vec{r}) = n_\infty \exp\left(-\frac{e\phi(\vec{r})}{k T_i}\right). \quad (2)$$

However, if the ions are nearly collisionless as they fall into the potential hole near the particle, there is the tendency for the density to decrease due to the increase in velocity. This is counteracted by the focussing effect in any convex region of the sheath where the angular momentum about the center of the particle is important. This microcanonical (fixed total energy) aspect of the ion distribution is critical for

plasmas in contact with nearly planar solid surfaces where the ion density does actually decreases as one approaches the surface, although not as much as the drop in electron density. A comprehensive study of the distribution of ions and electrons near particles based on Vlasov theory of Bernstein and Rabinowitz¹⁹ has been presented.¹⁸

The question of the ion energy as one moves into the vicinity of the solid particle must be estimated to some degree. In all cases the particle will charge negatively and be surrounded by a cloud of positive "space charge" due to the high velocity of the electrons compared to the ions. The particle is in essence acting as a catalyst for ion-electron recombination within the plasma. The recombined charges may either deposit neutrals on the particle or escape as a neutral gas. The kinetics of the recombination process creates an energy flow from the plasma to the particle that must be supplied continuously within the plasma bulk.

In order to proceed with the analysis without getting bogged down in details that are not pertinent to the main point, it is assumed that electrons and ions are both distributed by a Boltzmann law as given in Eqs.(1) and (2). The Poisson equation (PE) for the potential field ϕ due to a distribution of charge ρ is

$$\nabla^2 \phi(\vec{r}) = -\rho(\vec{r}) / \epsilon_0 \quad (3)$$

where SI units are used: namely, distance is in m, V is in volts (V), ρ is in C/m³, and the vacuum permittivity ϵ_0 is in C²/J m. Essential to solving the Debye shielding problem is the linearization of the electron and ion densities in terms of the potential field:

$$\begin{aligned} \rho_{sh}(\vec{r}) &= e(n_i(\vec{r}) - n_e(\vec{r})) \\ &= e \left[n_\infty \exp\left(-\frac{e\phi(\vec{r})}{kT_i}\right) - n_\infty \exp\left(\frac{e\phi(\vec{r})}{kT_e}\right) \right] \\ &\approx -e^2 n_\infty (1/kT_i + 1/kT_e) \phi(\vec{r}) \end{aligned} \quad (4)$$

where ρ is labeled with *sh* (sheath) to indicate that this charge density arises from the plasma region surrounding the particles. The rest of the charge density in the system is that trapped on the particles, which is denoted by ρ_p . The total charge density is

$$\rho = \rho_{sh} + \rho_p \quad (5)$$

The linearized PE for the whole plasma system is now obtained by combining Eqs. (3), (4), and (5),

$$\nabla^2 \phi = \lambda^{-2} \phi - \frac{1}{\epsilon_0} \rho_p, \quad (6)$$

where the Debye length λ is defined in terms of the individual electron and ion Debye lengths:

$$\begin{aligned} \lambda_e^2 &= \epsilon_0 k T_e / e^2 n_\infty, \\ \lambda_i^2 &= \epsilon_0 k T_i / e^2 n_\infty, \\ 1/\lambda^2 &= 1/\lambda_e^2 + 1/\lambda_i^2. \end{aligned} \quad (7)$$

In order to solve Eq.(6), boundary conditions (b.c.) must be imposed on the potential field. At large distance, the field must vanish. The boundary condition at each particle must be established in order to complete the solution.

The easy method to treat the charged particles is to take the limit of a point charge for each of the particles. Since it is assumed that the particles are small compared to the Debye lengths (Eq.(7)) this is not a concern, except that one must be careful to avoid the singular self-energies of the distributions. Thus the particle charge density is

$$\rho_p = \sum_n q_n \delta^3(\vec{r} - \vec{r}_n) \quad (8)$$

where the charge on each particle, q_n , must be connected to the potential b.c. to be used in the solution of the PE. This relation can be shown to be

$$q_n = 4\pi \epsilon_0 R_n \phi_n \quad (9)$$

where R_n denotes the particle radius and ϕ_n denotes the potential b.c. at that particle's surface. The specification of ϕ_n is the more fundamental quantity for the particle as it is the (negative) plasma floating potential and typically given by a formula like

$$\phi_p = (k T_e / e) \ln(4 v_i / v_e), \quad (10)$$

where v_i and v_e are mean velocities of the ions and electrons in the plasma bulk.

The solution of Eq.(6) can now be performed.²⁰ The Green's function for the PE,

$$G_o(\vec{r}, \vec{r}') = -1/4\pi|\vec{r} - \vec{r}'|, \quad (11)$$

$$\nabla_r^2 G_o(\vec{r}, \vec{r}') = \delta^3(\vec{r} - \vec{r}'),$$

is generalized to the Green's function for the homogeneous Helmholtz equation:

$$G_\lambda(\vec{r}, \vec{r}') = -\frac{\exp(-|\vec{r} - \vec{r}'|/\lambda)}{4\pi|\vec{r} - \vec{r}'|}, \quad (12)$$

$$(\nabla_r^2 - \lambda^{-2})G_\lambda(\vec{r}, \vec{r}') = \delta^3(\vec{r} - \vec{r}').$$

From this one can write the general solution to Eq.(6) as

$$\phi(\vec{r}) = -\frac{1}{\epsilon_0} \int d^3r' G_\lambda(\vec{r}, \vec{r}') \rho_p(\vec{r}') \quad (13)$$

The form of G_λ has been chosen to vanish at large distance as well as to satisfy the appropriate b.c. at each particle, as will be demonstrated shortly. Homogeneous solutions of the Laplace equation are not superimposed with the PE particular solution, because all fields are due to, or represented as, the superposition of real charges.

Substituting the superposition of particle charges in Eq.(8) into Eq.(13) gives the resultant potential throughout the plasma:

$$\phi(\vec{r}) = \frac{1}{4\pi\epsilon_0} \sum_n q_n \frac{\exp(-|\vec{r} - \vec{r}_n|/\lambda)}{|\vec{r} - \vec{r}_n|}. \quad (14)$$

This potential is everywhere negative relative to the plasma bulk, which of course is positive relative to confining physical boundaries, which are again negative relative to the bulk because of the wall sheaths. Consider the limit of the potential as $\vec{r} \rightarrow \vec{r}_n$ such that

$$|\vec{r} - \vec{r}_n| = R_n \quad (15)$$

where R_n is the radius of particle n. Because R_n / λ is very small, one finds:

$$\phi_{surface\ n} = \frac{1}{4\pi\epsilon_0} q_n / R_n , \quad (16)$$

which, by the definition of q_n in Eq.(9) is just the floating potential of the particle.

III. The Particle Interaction Energy

The total energy of the plasma-plus-particles system will be evaluated in enough generality to find the dependence on particle separation. The electrostatic energy is all that is needed and this can be found from the charge density. The total charge density in the system can be evaluated from the PE and Eq.(14), or from Eqs.(5), (8), and (13) to be:

$$\rho(\vec{r}) = \sum_n q_n \left(\delta^3(\vec{r} - \vec{r}_n) - \frac{1}{4\pi\lambda^2} \frac{\exp(-|\vec{r} - \vec{r}_n| / \lambda)}{|\vec{r} - \vec{r}_n|} \right) . \quad (17)$$

The integral over all space of this is zero, which insures neutrality.

The total electrostatic energy of the system will be evaluated in order to assess the existence of attraction of the Debye-shielded particles. In general the electrostatic energy is

$$\begin{aligned} \mathcal{E} &= \frac{1}{2} \frac{1}{4\pi\epsilon_0} \int d^3r \int d^3r' \rho(\vec{r}) \rho(\vec{r}') / |\vec{r} - \vec{r}'| \\ &= \frac{1}{2} \int d^3r \rho(\vec{r}) \phi(\vec{r}) \end{aligned} , \quad (18)$$

except that the singular self-interaction terms must be dropped that arise from the point-particle limit. The self-energy of the surface charge on a finite spherical particle is just $q_n^2 / 8\pi\epsilon_0 R_n$, which diverges as $R_n \rightarrow 0$ in the point charge limit, but is independent of the separations.

The electrostatic energy is evaluated for a pair of identical particles as a function of their separation $r = r_{12} = |\vec{r}_1 - \vec{r}_2|$. ϕ and ρ each consist of two terms to be identified with the two particles. These terms are exactly as written down in Eqs.(14) and (17). Substituting these into the second form in Eq.(18) and dropping the singular terms leaves the interaction energy:

$$\begin{aligned}
V(r_{12}) &= \int d^3r \rho_1(\vec{r}) \phi_2(\vec{r}) \\
&= \int d^3r \left(q_1 \delta^3(\vec{r} - \vec{r}_1) - \frac{q_1}{4\pi\lambda^2} \frac{\exp(-|\vec{r} - \vec{r}_1|/\lambda)}{|\vec{r} - \vec{r}_1|} \right) \\
&\quad \times \left(\frac{1}{4\pi\epsilon_0} q_2 \frac{\exp(-|\vec{r} - \vec{r}_2|/\lambda)}{|\vec{r} - \vec{r}_2|} \right)
\end{aligned} \tag{19}$$

which evaluates to be:

$$V(r) = \frac{1}{4\pi\epsilon_0} q^2 \frac{\exp(-r/\lambda)}{r} (1 - r/2\lambda) \tag{20}$$

where r is the separation of the particles. The particles are assumed identical, so the charges are the same. The non-trivial integral in Eq.(19) is evaluated by Fourier transformations. The zero of the interaction occurs at $r=2\lambda$, which shows that the Debye length might be considered a hard sphere radius for crystal packing while under pressure.

The interaction has a minimum whose properties are:

$$\begin{aligned}
r_{min} &= (1 + \sqrt{3})\lambda = 2.732\lambda \\
V_{min} &= -\frac{q^2}{4\pi\epsilon_0} \frac{1}{\lambda} 0.00872
\end{aligned} \tag{21}$$

The particle charge, q , is given in terms of radius and plasma potential by Eq.(9). Using this, q and V_{min} in Eq.(21) can be written in terms of “practical” quantities as:

$$\begin{aligned}
q/e &= 694.5 R_p \phi_p, \\
V_{min} &= -6.05 eV R_p^2 \phi_p^2 / \lambda, \\
\lambda &= 235 \mu m \sqrt{kT/e (in eV) / n_\infty (in 10^9 per cc)}.
\end{aligned} \tag{22}$$

where the particle radius R_p and the Debye length λ are measured in μm . The particle floating potential ϕ_p is in volts. From Eq.(22) one can evaluate the binding energy of a particle pair in terms of quantities which may be known about the plasma.

The temperature to be used in the expression for the Debye length probably should be the smaller ion temperature, which dominates the expression for λ as seen in Eq.(7).

IV. Discussion

Eq.(21) shows that the depth of the attractive well is about 1% of the repulsive Coulomb energy of the unscreened charged particles if separated by the Debye radius. An important question is how much kinetic energy the particles will possess compared to the binding energy. It seems a reasonable estimate that both the translational and internal temperature of the particles could be as much as the impact energy of the ions as they fall into the particle surface. However there are mechanisms involving the neutral background gas and radiation to cool the internal temperature of the particles well below this energy. In any case, an upper bound to the translational temperature in eV is on the order of the floating potential. Quantitative attempts to predict the particle temperature balance have been made.²¹ If one divides V_{min} in Eq.(22) by the floating potential, one can look at the dimensionless quantity

$$\Theta = 6.05 R_p^2 \phi_p / \lambda \quad (23)$$

as a measure of the binding ability (the larger than unity, the better). One can see that a particle radius of 10 μm , a Debye screening radius of 100 μm , and a floating potential of 10 V should be enough to give binding.

Another way to examine the energetics of the binding is to consider the fact that a particle of 10 μm radius, density 1 gm/cc, and moving at 1 cm/s has a kinetic energy of 1.31 keV. Other sizes, densities, and velocities can be found by scaling from this number.

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References

- ¹ H. Ikezi, Phys. Fluids **29**, 1764 (1986).
- ² J. H. Chu and Lin I, Phys. Rev. Lett. **72**, 4009 (1994).
- ³ H. Thomas, G. E. Morfill, V. Demmel, J. Goree, B. Feuerbacher, and D. Mohlmann, Phys. Rev. Lett. **73**, 652 (1994).
- ⁴ J. B. Pieper, J. Goree, and R. A. Quinn, J. Vac. Sci. Technol. **A 14**, 519 (1996).
- ⁵ G. E. Morfill and H. Thomas, J. Vac. Sci. Technol. **A 14**, 490 (1995).
- ⁶ M. Zuzic, H. M. Thomas, G. E. Morfill, J. Vac. Sci. Technol. **A 14**, 496 (1996).
- ⁷ H. M. Thomas and G. E. Morfill, J. Vac. Sci. Technol. **A 14**, 501 (1996).
- ⁸ Y. Hayashi and K. Tachibana, J. Vac. Sci. Technol. **A 14**, 506 (1996).
- ⁹ H. M. Thomas and G. E. Morfill, Nature, **379**, 806 (1996).
- ¹⁰ U. Mohideen, H. U. Rahman, M. A. Smith, M. Rosenberg, and D. A. Mendis, Phys. Rev. Lett. **81**, 349 (1998).
- ¹¹ K. Takahashi, T. Oishi, K. Shimomai, Y. Hayashi, and S. Nishino, Phys. Rev. E **58**, 7805 (1998).
- ¹² M. S. Barnes, J. H. Keller, J. C. Forster, J. A. O'Neill, and D. K. Coultas, Phys. Rev. Lett. **68**, 313 (1992).
- ¹³ F. Melandso and J. Goree, J. Vac. Sci. Technol. **A 14**, 511 (1996).

¹⁴ H. C. Lee, D. Y. Chen, and B. Rosenstein, Phys. Rev. E **56**, 4596 (1997).

¹⁵ H. H. Hwang and M. J. Kushner, J. Appl. Phys. **82**, 2106 (1997).

¹⁶ S. J. Choi and M. J. Kushner, J. Appl. Phys. **75**, 3351 (1994).

¹⁷ F. F. Chen, "Introduction to Plasma Physics and Controlled Fusion," Vol. 1, Plenum, NY, NY, p290-ff. (1988).

¹⁸ J. E. Daugherty, R. K. Porteous, M. D. Kilgore, and D. B. Graves, J. Appl. Phys. **72**, 3934 (1992).

¹⁹ I. Bernstein and I. Rabinowitz, Phys. Fluids **2**, 112 (1959).

²⁰ P. M. Morse and H. Feshbach, "Methods of Theoretical Physics," Chs. 7, 10, and 11, McGraw-Hill Book Co., New York, NY, 1953.

²¹ D. B. Graves, J. E. Daugherty, M. D. Kilgore, and R. K. Porteous, Plasma Sources Sci. Technol. **3**, 433 (1994).

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