# Dipolar interaction in a colloidal plasma

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The dipole-dipole interaction between macroscopic grains in a plasma is calculated. The presence of a plasma medium shields the Coulomb grain interactions as well as necessitates that nonzero temperature effects be accounted for. The resulting electrostatic but not so much the Helmholtz free energy shows overshooting when equal strength parallel dipoles align with or are perpendicular to the line joining their centers. More striking is the appearance of a short range attractive well interaction for angles near $\pi/3$. The contribution of the dipole-dipole to the total interaction in so-called plasma crystals has become increasingly recognized.

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## I. INTRODUCTION

Micron size dust particles, or grains charged by plasma have been observed to form crystalline phases as well as isolated and agglomerated pairs in low temperature plasmas [1,2]. Such grains are common contaminants in low pressure (100's mtorr), partially ionized (ion density $10^9 \leqslant n_i \leqslant 10^{11}\ \mathrm{cm}^{-3}$) plasma processing rf electrical glow discharges. The grains charge negatively and particles microns in size (radius *fraction* $\mu$m$\leqslant a \leqslant 100\ \mu$m) can have up to tens of thousands of elementary charges, $10^3$–$10^5$ electron charges according to various estimates. The negative charge balances the flux of electrons and ions to the grain surface generating floating potentials of $(1.5\text{–}3)T_e$, the electron temperature being in the range (2–5) eV. In plasma chambers these structures are found at the edge of the plasma above a negative dc self-biased electrode where an electric field exists. The field balances ion drag and gravitational forces thus keeping the grains afloat. In this region the plasma temperature and Debye length are characterized by the electron values, with $\lambda_{De} \simeq 4\times 10^{-2}$ cm. These structures should also form in the bulk plasma which is characterized by zero electric field, the ion temperature and the ion Debye length $\lambda_{Di} \simeq 5\times 10^{-3}$ cm. In plasma crystals the grain density is of the order $n_g \simeq 10^4\ \mathrm{cm}^{-3}$ while the grain and ion temperatures are approximately room temperature, $T_g \leqslant T_i \simeq 300$ K. A simple estimate shows that since grain densities are $\leqslant 10^6\ \mathrm{cm}^{-3}$ in the lattice, they can be treated as distinct entities.

The assembly of a colloidal plasma crystal is viewed here as starting from a configuration with each grain initially uncharged and infinitely separated in a neutral plasma background of mobile singly charged ions and electrons. The grains are treated as ''external'' to the plasma gas, not as additional constituents of the screening medium. Due to the difference between ion and electron mobilities, the grains become charged, typically in a fraction of a second. The response of the plasma particles is treated in the adiabatic approximation which assumes that at any time the plasma particles take on the configuration they would have if the grains were frozen into their instantaneous positions (infinite grain mass). The plasma gas distributes itself so as to shield or screen the fields produced by the grain distribution. Thus, as the grains execute their comparatively sluggish motion, the nimble plasma particles are continually redistributing themselves so as to cancel out the long range part of the grain field, yielding an effective grain field that is short ranged.

The final lattice configuration is obtained by allowing the grains to slowly and isothermally approach each other while maintaining the volume of the system constant. At these low temperatures the energy, both potential and kinetic, of the background plasma is comparable to the energy of the grains, and must be taken into account in discussing the stability of lattices. By fixing the plasma temperature $T$, the Helmholtz free energy acts as the ''effective potential energy'' for the system.

The importance of the dipole interaction in these structures has become increasingly recognized [3]. Under some conditions, deformed and oriented three dimensional close packed lattices of bcc, fcc, or hcp type, but mostly triangular arrays of vertical chains of grains are seen.These unusual phases have recently been explained as due to dipole-dipole interactions. Detailed lattice structures and highly complex phase diagrams have been calculated based on this interaction [4]. At low dipole strengths, the dipole interaction is manifest in the preferred orientation of the cubic lattices. At intermediate strengths, the triangular and hcp lattices begin to coexist with the preferred cubic lattices. At still higher strengths, the triangular array of vertical chains is preferred. The stability of these lattices against excitations, namely compression and vibration, has also been investigated. Other studies, using the same dipole interaction, have addressed waves in dusty plasma crystals [5]. The effective two-particle interaction has been incorporated into a lattice wave dispersion relation. Compared to the zero dipole case, the sound speed is reduced from that of a lattice with purely monopole interactions. The reduction is attributed to a long-range dipole contribution which arises as a result of plasma screening.

In these studies, point grains of equal size have been assumed. In this limit, one may expand the interaction, terminating at the dipole terms. An examination of this expansion, however, reveals that not all dipole terms have been retained. Since the missing terms are long-range terms associated with the reduced sound speed, they should be included. More importantly, the point grain approximation is justified when the ratio of particle size to lattice spacing is small. There is,

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however, an additional independent length parameter in the system, namely, the ratio of particle size to Debye length which is strickly zero in the point grain limit. In recent experiments on the intergrain coupling in dusty plasma Coulomb crystals [6], this parameter is of order unity and, as will be shown in this work, has a strong effect on the potential and free energy curves. Additionally, the dipole strength is extremely sensitive to the grain size, a cubic dependence in grain size $a$ in presence of an external field $E_0$, according to the simple approximate expression, $|p|=a^3E_0$. Since this is one of the parameters defining the phase diagram, in addition to the lattice spacing and temperature, and since energy differences between different phases are small, an improved expression for this interaction is desirable.

A finite grain expression for the dipole interaction energy should reduce to the point grain expression when the grain size tends to zero, which in turn should reproduce the well known vacuum expression, i.e., the no-screening limit, when the Debye length is infinite. The actual ''available energy'' in a system at constant temperature is always a competition between high entropy and low internal energy. Consequently, the effective interaction energy of the system is the Helmholtz free energy. An analytic expression for the free energy is important because it not only gives the effective interaction but also enables the derivation of the complete thermodynamics of the system.

In this work the dipole interaction in a colloidal plasma is calculated. The monopole interaction has been considered previously and is presented elsewhere [7]. Section II describes the physical system under consideration and formulates the problem. In the following two sections, the electrostatic potential energy and Helmholtz free energy for dipolar interactions are obtained both for finite as well as point grains. The final section presents a discussion of the results.

## II. COLLOIDAL PLASMA SYSTEM

For the electrostatics of $N_g$ grains of radius $a$ and a variable charge $Q$ in a plasma, we treat the plasma medium, consisting of electrons and singly charged ions in the classical equilibrium fluid approximation. We consider situations where the Debye length is much smaller than the dimensions of the system and such that a significant number of plasma particles collect around each grain. In the neighborhood of a charged grain, the plasma is perturbed. We also consider situations where the perturbed plasma volume is small in comparision with the unperturbed plasma resevoir. The electron and ion densities are then distributed according to the Maxwell-Boltzmann relation

$$n_{i(e)}=\overline{n}_{i(e)}\exp(\mp e\tilde{\Phi}/k_BT), \tag{1}$$

where a bar over particle densities denotes an average, subscripts $i$ and $e$ refer to ions and electrons respectively, $e$ is the absolute value of the elementary charge, $T$ represents the common electron-ion temperature, $k_B$ is Boltzmann's constant and $\tilde{\Phi}$ the total electrostatic potential consisting of the plasma particle potential and any externally applied potential $\tilde{\Phi}=\tilde{\Phi}^p+\tilde{\Phi}^{ext}$. In what follows, we shall be primarily interested in a constant external uniform electric field.

The system is completely specified with the addition of Poisson's equation

$$\nabla^2\tilde{\Phi}=-4\pi\tilde{\rho}^{ext}-4\pi e(n_i-n_e), \tag{2}$$

where $\tilde{\rho}^{ext}$ is the external charge density which gives rise to $\tilde{\Phi}^{ext}$. If the plasma particle average potential energy is much smaller than the average kinetic energy, we may expand the particle densities to linear order in the total potential. By separating the individual contributions, one obtains an equation for the external potential $\nabla^2\tilde{\Phi}^{ext}=-4\pi\tilde{\rho}^{ext}$, and an equation for the plasma particle potential

$$(\nabla^2-k^2)\tilde{\Phi}^p=-4\pi e(\overline{n_i}-\overline{n_e})+k^2\tilde{\Phi}^{ext}. \tag{3}$$

In this equation $k^2=4\pi e^2(\overline{n_i}+\overline{n_e})/(k_BT)$ is the square of the inverse Debye length. Assuming *overall* charge neutrality, the constant term in the latter equation, may be related to the grain charge. In an impermeable grain model, the mean plasma charge excess is expressed in terms of the total charge on all grains by $e(\overline{n_i}-\overline{n_e})=-n_gQ/(1-4\pi a^3n_g/3)\simeq-n_gQ$, with $n_g$ denoting the grain density in the plasma grain mixture. Defining a mean background plasma potential $\overline{\phi}\equiv4\pi e(\overline{n_i}-\overline{n_e})/(2k^2)$ and shifting the potentials $\Phi^p=\tilde{\Phi}^p-\overline{\phi}$ and $\Phi^{ext}=\tilde{\Phi}^{ext}-\overline{\phi}$, the constant term drops out leaving for the plasma potential

$$(\nabla^2-k^2)\Phi^p=k^2\Phi^{ext}. \tag{4}$$

For the volumetric source term on the right-hand side of Eq. (4), we shall take $\Phi^{ext}=-E_0r\cos(\theta)$, representing a uniform external field in the (arbitrary) $z$ direction relative to the mean background.

It would seem that one must solve an inhomogeneous linear partial differential equation subject to boundary conditions on the grain surfaces and at infinity. The complete solution would then consist of a superposition of the homogeneous and a particular solution. It may be seen though, that due to the perfect plasma shielding property, only the homogeneous solution survives. Provided $\Phi^{ext}$ is such that $\nabla^2\Phi^{ext}=0$, Eq. (4) may be rewritten as

$$\nabla^2(\Phi^p+\Phi^{ext})-k^2(\Phi^p+\Phi^{ext})=0. \tag{5}$$

This condition poses no restriction, however, since any $\Phi^{ext}$ may be expanded in the complete set of eigenfunctions of the Laplacian operator, namely, in terms of spherical harmonics and powers of $r$, if spherical coordinates are used. By linearity, the solution for $N_g$ grains is the superposition of $N_g$ single grain solutions $\Phi=\Phi^p+\Phi^{ext}=\Sigma_j\phi_j$. For the system boundary conditions, we require $\Phi$ tend to zero infinitely far away from all grains for *any* configuration, as well as require that, if all grains are infinitely far from each other, the individual potentials tend to zero at large distances. Under the specified boundary conditions the individual grain potentials are given by the solution to the Helmholtz wave equation with imaginary wave vector $\kappa=ik$

$$\Phi=\Phi^p+\Phi^{ext}=\sum_{j=1}^{N_g}\sum_{n=0}^{\infty}B_{jn}h_n^{(1)}(\kappa R_j)P_n(\cos\Theta_j), \tag{6}$$

where and $(R_j,\Theta_j)$ are spherical coordinates relative to the individual grain centers, $h_n^{(1)}$ is a Hankel function representing outgoing waves at infinity, $P_n$ is a Legendre polynomial of order $n$, and the coefficients $B_{jn}$ are to be determined from the boundary condition on the grain surfaces.

Neglecting monopole contributions, the potential on the surface of any grain is the dipole potential, $-E_0 a\cos\theta$, of the uniform external field,

$$-E_0\cos\Theta_i=\sum_{j=1}^{N}\sum_{n=0}^{\infty}B_{jn}h_n^{(1)}(\kappa R_j)P_n(\cos\Theta_j),\qquad i=1,\ldots,N. \tag{7}$$

The above linear system of equations may be solved under varying degrees of approximation. Here we consider independent grains, i.e., all induced potentials are negligible at the location of grain $i$, except the ith potential itself. In this approximation the total potential is

$$\Phi=-\sum_{j=1}^{N_g}a^3\mathbf{E}_0\cdot\hat{R}_j\frac{e^{ka}}{(1+ka)}\frac{(1+kR_j)e^{-kR_j}}{R_j^2}, \tag{8}$$

where $\hat{\mathbf{R}}_j\cdot\mathbf{E}_0=E_0\cos\Theta_j$ is the component of $E_0$ in the $\hat{\mathbf{R}}_j$ direction.

It is well known that an alternative to the eigenfunction technique for solving boundary value problems involves solving the inhomogeneous equation for homogeneous boundary conditions for a point source at some point inside the surface. The solution is then obtained by integrating the Green's function over the space inside and on the surface. In the limit of independent charged metallic point grains in a constant external field, Eq. (5) reduces to

$$(\nabla^2-k^2)\Phi=4\pi\sum_i\mathbf{p}\cdot\nabla\delta(\mathbf{r}-\mathbf{r}_i). \tag{9}$$

Denoting the distance between the observation point, $\mathbf{r}$, and the source point, $\mathbf{r}'$, by $R\equiv|\mathbf{r}-\mathbf{r}'|$, the appropriate Green's function for this equation satisfying homogeneous boundary conditions $(G=0)$ at infinity is $G(\mathbf{r},\mathbf{r}')=\exp(-kR)/R$. By superposition, the total potential is

$$\Phi=\sum_j\mathbf{p}_j\cdot\hat{\mathbf{R}}_j(1+kR_j)\frac{\exp(-kR_j)}{R_j^2}. \tag{10}$$

In obtaining this potential, use has been made of the properties of the $\delta$ function and its first derivative. In order that the independent finite grain solution reduce to the point grain solution, we must identify $\mathbf{p}=-a^3\mathbf{E}_0$, as $a\to 0$. Point grains are independent since *all* distances are "far." This limit is a special case of the result that the integral of an electric field over a volume completely enclosing a charge density is equal to $-4\pi\mathbf{p}/3$ [8]. The vacuum point grain limit, $k\to 0$, reduces to the expected expression $\Phi=\Sigma_i\mathbf{p}_i\cdot\hat{\mathbf{R}}_i/R_i^2$.

### III. ELECTROSTATIC POTENTIAL ENERGY

From electrostatics, the electrical interaction energy of a system of charged particles can be written as half the sum of the product of each charge and the potential of the field at the position of that charge due to all other charges

$$U=\tfrac{1}{2}\int_V\rho\Phi\,dV+\tfrac{1}{2}\int_S\sigma\Phi\,dA. \tag{11}$$

The (self-consistent) volume charge density is determined from Poisson's equation $\rho=-1/(4\pi)\nabla^2\Phi=-k^2/(4\pi)\Phi$, and the surface charge density on the grains by $\sigma=\Sigma_i -1/(4\pi)\partial\Phi\partial R_i$ evaluated at the grain surfaces, $R_i=a$. For point grains the delta function dipole sources are volumetric. The free space equation above is permissible since the background plasma medium is linear, so that $\rho$ and $\Phi$ are linearly related. Denoting the position vectors relative to the grain centers by $\mathbf{R}_i$, the separation vector between two grains $i$ and $j$ is then $\mathbf{R}_{ij}=\mathbf{R}_i-\mathbf{R}_j$. To obtain the electrostatic energy, we integrate over the full space by fixing the origin of coordinates on the center of grain $i$ and letting $\mathbf{R}_i\equiv\mathbf{r}-\mathbf{r}_i=R_{ij}\boldsymbol{\rho}$ and $\mathbf{R}_j\equiv\mathbf{r}-\mathbf{r}_j=\mathbf{R}_{ij}+R_{ij}\boldsymbol{\rho}$. The norm of these two vectors is $R_i=R_{ij}\rho$ and $R_j=R_{ij}|\hat{\mathbf{n}}+\boldsymbol{\rho}|=R_{ij}u$ respectively. The vector $\mathbf{u}$ has the norm $u=|\hat{\mathbf{n}}+\boldsymbol{\rho}|=\sqrt{(1+\rho^2+2\rho\cos\gamma)}$ with $\hat{\mathbf{n}}=\mathbf{R}_{ij}/R_{ij}$ a unit vector parallel to the intergrain axis from $(j)$ to $(i)$. The azimuthal dependence of the integrand is no more complicated than a cos or a sin factor. In terms of the new independent variables $\rho$ and $u$, the arguments of the exponential functions are simple, enabling an analytic evaluation of the integrals. Additional details regarding the coordinates used appear in the appendix. The potential energy of a Debye shielded dipole in the field of a second Debye shielded dipole is found to be

$$U_{ij}^d=\frac{e^{-kR_{ij}}}{2(ka)^3(1+ka)^2R_{ij}^3}[U1_{ij}^d\mathbf{p}_1\cdot\mathbf{p}_2+U2_{ij}^d\mathbf{p}_1\cdot\hat{\mathbf{R}}_{ij}\mathbf{p}_2\cdot\hat{\mathbf{R}}_{ij}], \tag{12}$$

where

$$U1_{ij}^d=\alpha+\alpha kR_{ij}+(ka)^3e^{2ka}(kR_{ij})^2,$$
$$U2_{ij}^d=-3\alpha-3\alpha kR_{ij}-\beta(kR_{ij})^2+(ka)^3e^{2ka}(kR_{ij})^3, \tag{13}$$

with

$$\alpha=[(1+ka)-e^{2ka}(1-ka)][3+3ka+(ka)^2],$$
$$\beta=3+6ka+4(ka)^2+(ka)^3-e^{2ka}[3-2(ka)^2]. \tag{14}$$

In the point grain limit, $a\to 0$, the electrostatic dipole potential energy becomes

$$U_{ij}^d=-\frac{e^{-kR_{ij}}}{2R_{ij}^3}[(-2-2kR_{ij}+k^2R_{ij}^2)\mathbf{p}_1\cdot\mathbf{p}_2+(6+6kR_{ij}+k^2R_{ij}^2-k^3R_{ij}^3)\mathbf{p}_1\cdot\hat{\mathbf{R}}_{ij}\mathbf{p}_2\cdot\hat{\mathbf{R}}_{ij}]. \tag{15}$$

In the weak screening or vacuum limit, $k\to 0$, we recover the well known dipole interaction energy [8]

$$U_{ij}^d=\frac{\mathbf{p}_1\cdot\mathbf{p}_2-3\mathbf{p}_1\cdot\hat{\mathbf{R}}_{ij}\mathbf{p}_2\cdot\hat{\mathbf{R}}_{ij}}{R_{ij}^3}. \tag{16}$$

An expression for the dipole electrostatic energy has been derived and used to study the phase diagram of dusty plasma crystals ( [4]). The expression assumed point parallel dipoles of equal strength. In our notation their result is

$$U_{ij}^{d}=-p_0^2\frac{e^{-kR_{ij}}}{R_{ij}^3}\left[(-1-1kR_{ij})+\left(3+3kR_{ij}+\frac{k^2R_{ij}^2}{2}\right)\cos\theta_{ij}^2\right].$$

The angle $\theta_{ij}$ is the angle between the orientation of the dipoles and the line between grain centers. When compared to the above result, this expression neglects long range terms. The expression derived by these authors corresponds to the electrostatic dipole energy of a point dipole in presence of a second Debye shielded point dipole. The missing terms arise from the energy of the Debye sheath around the first dipole in presence of the second Debye shielded point dipole. This additional long range contribution arises naturally if one uses the self-consistent charge density determined from Poissons equation in the energy equation in analogy with the Thomas-Fermi statistical model of the atom.

Figure 1 displays the normalized (to ${p_0}^2k^3$) shielded dipole–shielded dipole electrostatic potential energy as a function of free intergrain spacing. Equal strength parallel dipoles are assumed for illustration purposes. For dipoles parallel to the line between centers, Fig. 1(a) with $\theta_{ij}=0$, and below approximately $ka=1$, the energy is predominantly negative but displays overshooting above zero. The $ka=1$ case, for example, displays essentially a repulsive hump with a deep well at very short distances. For higher values of $ka$, the energy becomes strictly positive. For $\theta_{ij}=\pi/2$, Fig. 1(b), this behavior is reversed. For angles near $\pi/3$, in the transition region between predominantly attractive and predominantly repulsive and for low $ka$ values, a short range attractive well structure appears which is strongly repulsive at very small free intergrain separation. This indicates that nearest neighbor dipoles on separate planes (intergrain axis $\simeq\pi/3$ with respect to dipole orientation) tend to seek a stable attractive equilibrium separation. Overshooting as well as attractive well structures are purely sheath effects.

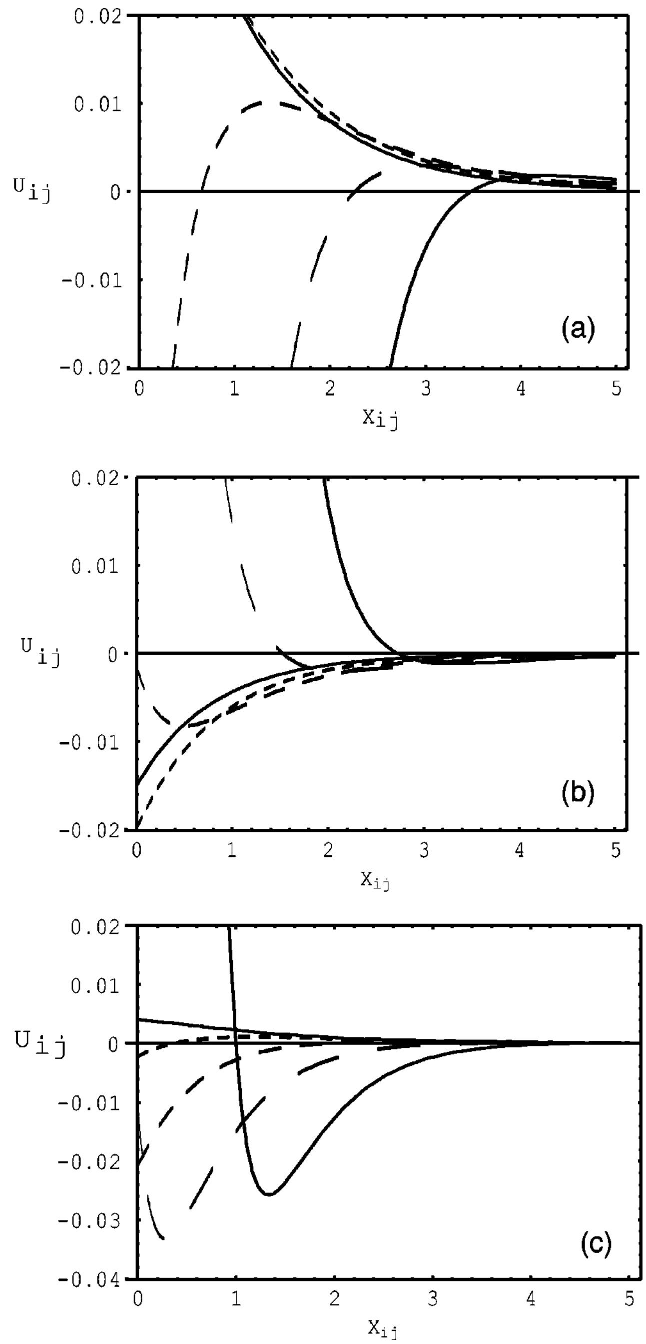


FIG. 1. Pair electrostatic interaction energy $U_{ij}$ normalized to $k^3p_0^2$ as a function of free intergrain spacing, $X_{ij}=R_{ij}-2a$ normalized to $\lambda_D=k^{-1}$ for $ka=0,0.5,1,1.5,2$ (solid to decreasing dashing to solid) for (a) $\theta_{ij}=0$, (b) $\theta_{ij}=\pi/2$, and (c) $\theta_{ij}=\pi/3$.

## IV. HELMHOLTZ FREE ENERGY

In taking the plasma temperature to be a fixed value, we are effectively assuming the background species are in contact with a large resevoir at the plasma temperature, which remains uniform in space and constant in time. The *available work at constant temperature* or the (Helmholtz) free energy thus acts as the effective potential energy for the system. Part of the energy is supplied by a change in the configuraton of the system and charging and part is supplied by heat that flows into the system from the resevoir that maintains the temperature constant. At thermodynamic equilibrium, the free energy takes on a minimum value corresponding to the stable configuration of the system.

For the calculation of the free energy, we note that the plasma particles are of two kinds, mobile particles in the plasma and immobile particles on grain surfaces. The system of plasma and grains thus conserves total particle number. Any volume changes associated with a change of grain configuration may be neglected. Under these circumstances, the Helmholtz free energy may be obtained from the Coulomb energy by integrating the thermodynamic relation $\partial(F/T)/\partial T=-U/T^2$. The constant of integration must be taken as zero, since when $T\rightarrow\infty$ we must have $F=F_{id}$, the ideal free energy corresponding to the fully non-interacting or uncorrelated plasma [9]. The deviation from ideality includes the plasma particle and grain contributions. Only the latter depends on the grain configuration. Expressing the temperature in terms of the wave vector, the free energy of grain interaction may be obtained from the electrostatic interaction energy from

$$k^2 F_{ij} - k_{id}^2 F_{ij}^{id} = 2\int_0^k U_{ij}(k')k'dk'. \tag{17}$$

Proceeding as before on finds the rather complicated analytical result

$$F_{ij}^d = (F1_{ij}^d - F1_{ij}^{d0})\mathbf{p}_1\cdot\mathbf{p}_2 + (F2_{ij}^d - F2_{ij}^{d0})\mathbf{p}_1\cdot\hat{\mathbf{R}}_{ij}\mathbf{p}_2\cdot\hat{\mathbf{R}}_{ij}, \tag{18}$$

where

$$F1_{ij}^d = -\frac{3+ka}{ka^3R_{ij}^3e^{kR_{ij}}} - \frac{S_1e^{2ka-kR_{ij}}}{ka^4(1+ka)(2a-R_{ij})^2R_{ij}^3} - \frac{S_2e^{-2+R_{ij}/a}}{a^5R_{ij}^3}E_i((1+ka)(2a-R_{ij})/a) + \frac{e^{R_{ij}/a}(a-R_{ij})}{a^3R_{ij}^3}E_i(-(1+ka)R_{ij}/a), \tag{19}$$

and

$$F2_{ij}^d = \frac{S_3e^{-kR_{ij}}}{ka^3R_{ij}^3} + \frac{S_4e^{2ka-kR_{ij}}}{ka^5(1+ka)(2a-R_{ij})^3R_{ij}^3} + \frac{S_5e^{-2+R_{ij}/a}}{a^6R_{ij}^3}E_i((1+ka)(2a-R_{ij})/a) - \frac{S_6e^{R_{ij}/a}}{a^4R_{ij}^3}E_i(-(1+ka)R_{ij}/a). \tag{20}$$

The $S'$s are the polynomials in $R_{ij}, a, k$,

$$S_1 = -12a^3 - 20ka^4 + 12a^2R_{ij} + 26ka^3R_{ij} - 2k^2a^4R_{ij} - 3aR_{ij}^2 - 13ka^2R_{ij}^2 - 2k^2a^3R_{ij}^2 + 2k^3a^4R_{ij}^2 + k^2a^2R_{ij}^3 - k^3a^3R_{ij}^3 + kR_{ij}^4,$$

$$S_2 = 9a^3 - 9a^2R_{ij} + 3aR_{ij}^2 + R_{ij}^3,$$

$$S_3 = 9 + 4ka + 2kR_{ij} + k^2aR_{ij}, \tag{21}$$

$$S_4 = -72a^5 - 120ka^6 + 108a^4R_{ij} + 216ka^5R_{ij} - 12k^2a^6R_{ij} - 54a^3R_{ij}^2 - 166ka^4R_{ij}^2 + 4k^2a^5R_{ij}^2 + 9a^2R_{ij}^3 + 78ka^3R_{ij}^3 + 11k^2a^4R_{ij}^3 - 8k^3a^5R_{ij}^3 + 4k^4a^6R_{ij}^3 - 16a^2kR_{ij}^4 - 6k^2a^3R_{ij}^4 + 6k^3a^4R_{ij}^4 - 4k^4a^5R_{ij}^4 - 2kaR_{ij}^5 + k^2a^2R_{ij}^5 - k^3a^3R_{ij}^5 + k^4a^4R_{ij}^5 + kR_{ij}^6,$$

$$S_5 = 27a^4 - 27a^3R_{ij} + 12a^2R_{ij}^2 - 3aR_{ij}^3 - R_{ij}^4,$$

$$S_6 = 3a^2 - 3aR_{ij} + R_{ij}^2.$$

The lower limit of integration, $k=0$ contributes

$$F1_{ij}^{d0} = \frac{a[T_1ae^2 + T_2a^2e^{2+R_{ij}/a}E_i(-R_{ij}/a) - T_3e^{R_{ij}/a}E_i(2-R_{ij}/a)]}{(-2a+R_{ij})^2a^6e^2R_{ij}^3},$$
$$F2_{ij}^{d0} = \frac{[T_4ae^2 - T_5a^2e^{2+R_{ij}/a}E_i(-R_{ij}/a) + T_6e^{R_{ij}/a}E_i(2-R_{ij}/a)]}{(2a-R_{ij})^3a^6e^2R_{ij}^3}, \tag{22}$$

where

$$T_1 = 28a^4 - 34a^3R_{ij} + 15a^2R_{ij}^2 - R_{ij}^4,$$
$$T_2 = (a-R_{ij})(-2a+R_{ij})^2,$$
$$T_3 = (-2a+R_{ij})^2(9a^3 - 9a^2R_{ij} + 3aR_{ij}^2 + R_{ij}^3),$$
$$T_4 = -160a^6 + 292a^5R_{ij} - 220a^4R_{ij}^2 + 95a^3R_{ij}^3 - 18a^2R_{ij}^4 - 2aR_{ij}^5 + R_{ij}^6, \tag{23}$$
$$T_5 = (2a-R_{ij})^3(3a^2 - 3aR_{ij} + R_{ij}^2),$$
$$T_6 = (2a-R_{ij})^3(27a^4 - 27a^3R_{ij} + 12a^2R_{ij}^2 - 3aR_{ij}^3 - R_{ij}^4).$$

For the point grain limit we find

$$F=-\frac{k^2(-(1+kR_{ij})\mathbf{p}_1\cdot\mathbf{p}_2)+(3+3kR_{ij}+k^2R_{ij}^2)\mathbf{p}_1\cdot\hat{\mathbf{R}}_{ij}\mathbf{p}_2\cdot\hat{\mathbf{R}}_{ij}}{e^{kR_{ij}}R_{ij}^3}. \tag{24}$$

The weak screening limit result is identical to the one obtained for the electrostatic energy, as expected,

$$F=\frac{\mathbf{p}_1\cdot\mathbf{p}_2-3\mathbf{p}_1\cdot\hat{\mathbf{R}}_{ij}\mathbf{p}_2\cdot\hat{\mathbf{R}}_{ij}}{R_{ij}^3}. \tag{25}$$

Despite the complexity of the free energy expression for finite grains, it does not include the finite volume correction arising from the impenetrability of the grains. The correction is small for small $ka$ values. It has, however, been calculated and appears in the Appendix. All figures shown in this work include this correction.

Figure 2 shows the Helmholtz free energy. For $\theta_{ij}=0$ (and $\pi/2$). Some overshooting still occurs particularly for large $ka$ values. The attractive well found before for $\theta_{ij}=\pi/3$ persists with the equilibrium separation shifting to lower distances. The depth of the well has decreased by roughly a factor of 5, however. For finite temperature systems the free energy is the more relevant quantity to calculate as it determines the effective available energy in the system to do work.

## V. DISCUSSION

In this work the Debye-shielded dipole-dipole interaction for finite polarized grains in a plasma has been calculated. The mechanism for grain polarization has not been considered; it could arise due to the presence of an external field, finite ion flows, as well as a plasma inhomogeneity. For the system of $N_g$ grains only the simplest boundary condition, namely independent grains, has been used. This approximation allows the total potential for $N_g$ grains to be obtained from a simple superposition of single grain solutions where the single grain potential is determined from the Poisson equation for one grain together with the corresponding single grain boundary conditions. Despite this, the finite grain expressions are fairly complex. One could go beyond independent grains and consider more complex boundary conditions, taking into account the induced fields of all grains on the surface of each grain. The resulting expressions would then carry information concerning the configuration of all grains and show great complexity. Mathematically, this would be treated by solving a linear system of $N_g$ equations. One should be aware, however, that even the potential fails to possess a closed form solution, being expressible as an infinite series only. Another approximation made in this work is the plasma approximation in which the product $ka$ is small, so that a large number of plasma particles participate in the shielding of each grain. While the size of the errors incurred by this approximation have not been calculated for the dipole interaction, it is known that in the monopole case, with proper account of the boundary conditions on spherical grains, to leading order the potential goes like $ka$ with additional terms proportional to $(ka)^2$ [10]. It is becoming increasingly recognized that in order to understand plasma crystal structures both monopole and dipole interactions must be taken into account.

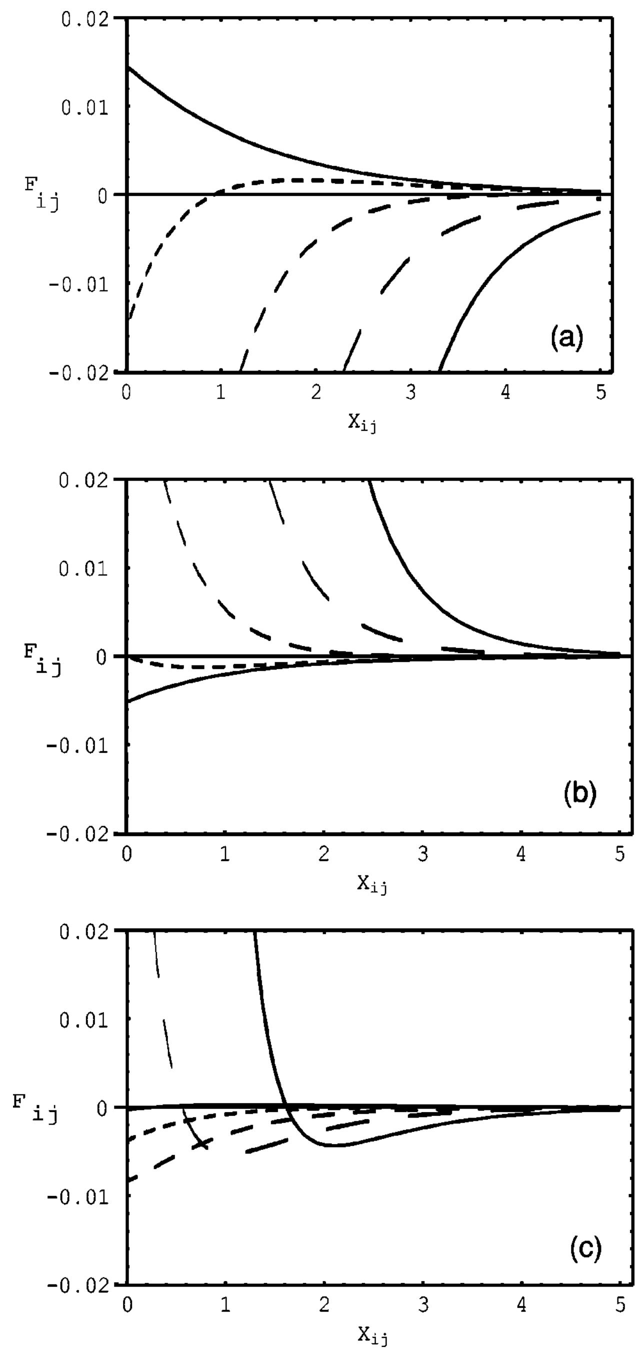


FIG. 2. Pair Helmholtz interaction energy $F_{ij}$ normalized to $k^3p_0^2$ as a function of free intergrain spacing, $X_{ij}=R_{ij}-2a$ normalized to $\lambda_D=k^{-1}$ for $ka=0,0,5,1,1.5,2$ (solid to decreasing dashing to solid) for (a) $\theta_{ij}=0$, (b) $\theta_{ij}=\pi/2$, and (c) $\theta_{ij}=\pi/3$.

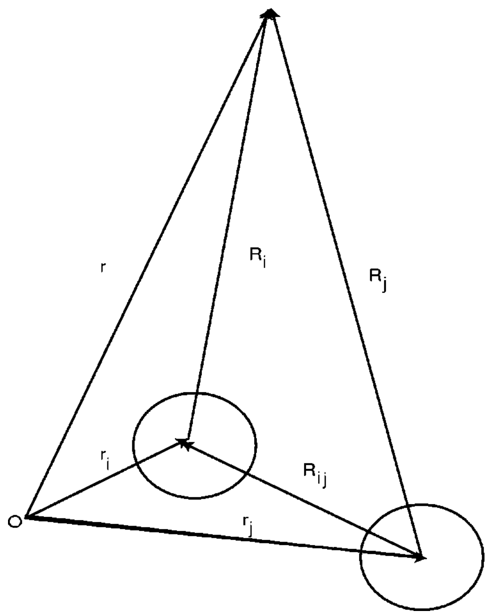


FIG. 3. CAPTION

## ACKNOWLEDGMENTS

The symbolic software system MATHEMATICA developed by Stephen Wolfram was used to obtain the results presented as well as to perform various checks of the theory. This work was supported in part by the ''Colloidal Plasmas'' research network of the European Commission.

## APPENDIX

In this appendix we present the evaluation details of the electrostatic energy [Eq. (11)] and free energy [Eq. (17)]. The volume correction to these energies arising from finite impenetrable grains is also given.

For the full space integration appearing in Eq. (11) we use the coordinates displayed in the following diagram (Fig. 3). The origin is first shifted to the center of grain $i$, assumed spherical. Relative to grain $i$ the position of grain $j$ is $\mathbf{R}_j = \mathbf{R}_{ij} + \mathbf{R}_i$. A right handed Cartesian system centered on grain $i$ is chosen with the $z$ axis parallel to the line joining grain centers in the direction from $j$ to $i$. With respect to this system

$$\mathbf{p}_i \cdot \mathbf{R}_i = p_{ix} R_i \sin\theta_i \cos\phi_i + p_{iy} R_i \sin\theta_i \sin\phi_i + p_{iz} R_i \cos\theta_i , \tag{A1}$$

$$\mathbf{p}_j \cdot \mathbf{R}_j = \mathbf{p}_j \cdot \mathbf{R}_{ij} + p_{jx} R_i \sin\theta_i \cos\phi_i + p_{jy} R_i \sin\theta_i \sin\phi_i + p_{jz} R_i \cos\theta_i .$$

In this equation $R_i$, $\theta_i$, and $\phi_i$ are spherical polar coordinates relative to the center of grain $i$. We next transform to new independent variables $\rho$, $u$ defined by

$$\mathbf{R}_i = \frac{\mathbf{R}_i}{R_{ij}} R_{ij} \equiv \boldsymbol{\rho} R_{ij} , \tag{A2}$$

$$\mathbf{R}_j = \mathbf{R}_{ij} + R_{ij} \boldsymbol{\rho}.$$

Thus, $\mathbf{R}_i = R_{ij}\boldsymbol{\rho}$ and $\mathbf{R}_j = R_{ij}\mathbf{u}$, where $u = |\hat{\mathbf{n}} + \boldsymbol{\rho}| = (1+\rho^2 + 2\rho\cos\theta_i)^{1/2}$ with $\hat{\mathbf{n}} = \mathbf{R}_{ij}/\mathbf{R}_{ij} = \hat{\mathbf{z}}$. Finally we let $x = \cos\theta_i$. Then as $x$ varies between $-1$ and $+1$, $u$ varies between $|1-\rho|$ and $|1+\rho|$. In terms of the new variables, the volume integration over any $\Psi(\rho, u, \phi_i)$ expressed in the new independent variables, becomes

$$\int d^3 r \Psi \rightarrow R_{ij}^3 \int_0^\infty \rho d\rho \int_{|1-\rho|}^{|1+\rho|} u du \int_0^{2\pi} d\phi_i \Psi$$
$$= R_{ij}^3 \left( \int_0^1 \rho d\rho \int_{1-\rho}^{1+\rho} u du + \int_1^\infty \rho d\rho \int_{\rho-1}^{1+\rho} u du \right) \int_0^{2\pi} \Psi d\phi_i . \tag{A3}$$

The arguments of the exponentials are particularly simple, enabling an analytic evaluation in terms of $\rho$ and $u$. The resulting integrand in $\rho$, after the $u$ and $\phi_i$ integrations have been carried out, has a finite discontinuity at $\rho=1$; the integral converges, however.

The electrostatic energy integrations are reduced to integrals of the type

$$\int P_m(x) e^{ax} dx = \frac{e^{ax}}{a} \sum_{k=o}^{m} (-1)^k \frac{P^{(k)}(x)}{a^k},$$

where $P_m(x)$ is a polynomial in $x$ of degree $m$ and $P^{(k)}(x)$ is the $k$th derivative of $P_m(x)$ with respect to $x$. For the Helmholtz free energy one simply integrates the electrostatic energy with respect to $k$. In this integration, integrals of the type $\int e^{ax}/x dx = E_i(ax)$ are encountered. While straightforward to evaluate, these integrals can become very tedious. Note that in the volume correction to the electrostatic energy the $\rho$ integration ranges from 0 to $a/R_{ij}$ and since the upper limit is always less than 1, only the first integral in Eq. (A3) contributes. For two grains the volume correction (minus sign displayed explicitly) to be added to Eq. (12) is

$$U_{ij}^{d(vol)} = \frac{-\gamma[(1+kR_{ij})\mathbf{p}_i \cdot \mathbf{p}_j - (3+3kR_{ij}+k^2R_{ij}^2)\mathbf{p}_i \cdot \hat{\mathbf{R}}_{ij} \mathbf{p}_j \cdot \hat{\mathbf{R}}_{ij}]}{2kae^{kR_{ij}}(1+ka)^2 R_{ij}^3}, \tag{A4}$$

where

$$\gamma = -2 + 2e^{2ka} - ka - 3kae^{2ka} + 2k^2a^2e^{2ka}.$$

Similarly, the volume correction to the Helmholtz free energy is

$$F_{ij}^{d(vol)} = F1_{ij}^{d(vol)} \mathbf{p}_1 \cdot \mathbf{p}_2 + F2_{ij}^{d(vol)} \mathbf{p}_1 \cdot \hat{\mathbf{R}}_{ij} \mathbf{p}_2 \cdot \hat{\mathbf{R}}_{ij} , \tag{A5}$$

where

$$F1_{ij}^{d(vol)} = -\frac{-2a+R_{ij}}{a^3R_{ij}^3} + \frac{-2a-ka^2+R_{ij}}{a^3e^{kR_{ij}}(1+ka)R_{ij}^3} - \frac{e^{k(2a-R_{ij})}}{a^3(1+ka)(2a-R_{ij})^2R_{ij}^3}[-28aR_{ij}^2+7R_{ij}^3+4a^4k(1+kR_{ij})$$
$$+a^2R_{ij}(38+5kR_{ij})-2a^3(12+7kR_{ij}+k^2R_{ij}^2)] - \frac{24a^3-38a^2R_{ij}+28aR_{ij}^2-7R_{ij}^3}{a^3(2a-R_{ij})^2R_{ij}^3}$$
$$+\frac{7e^{-2+R_{ij}/a}(a-2R_{ij})E_i\left(\frac{(1+ka)(2a-R_{ij})}{a}\right)}{a^3R_{ij}^3} - \frac{7e^{-2+R_{ij}/a}(a-R_{ij})(2a-R_{ij})E_i\left(\frac{(1+ka)(2a-R_{ij})}{a}\right)}{a^4R_{ij}^3}$$
$$-\frac{e^{R_{ij}/a}(a^2-aR_{ij}+R_{ij}^2)E_i\left(-\frac{R_{ij}}{a}\right)}{a^4R_{ij}^3} + \frac{e^{R_{ij}/a}(a^2-aR_{ij}+R_{ij}^2)E_i\left(-\frac{(1+ka)R_{ij}}{a}\right)}{a^4R_{ij}^3}$$
$$-\frac{7e^{-2+R_{ij}/a}(a-2R_{ij})E_i\left(2-\frac{R_{ij}}{a}\right)}{a^3R_{ij}^3} + \frac{7e^{-2+R_{ij}/a}(a-R_{ij})(2a-R_{ij})E_i\left(2-\frac{R_{ij}}{a}\right)}{a^4R_{ij}^3} \quad \text{(A6)}$$

and

$$F2_{ij}^{d(vol)} = -\frac{7a^2-3aR_{ij}+R_{ij}^2}{a^4R_{ij}^3} - \frac{-144a^5+300a^4R_{ij}-264a^3R_{ij}^2+147a^2R_{ij}^3-49aR_{ij}^4+7R_{ij}^5}{a^4(2a-R_{ij})^3R_{ij}^3}$$
$$+\frac{-3aR_{ij}+R_{ij}^2+ka^3(4+kR_{ij})+a^2(7+kR_{ij})}{a^4e^{kR_{ij}}(1+ka)R_{ij}^3} + \frac{e^{k(2a-R_{ij})}}{a^4(1+ka)(2a-R_{ij})^3R_{ij}^3}(-49aR_{ij}^4+7R_{ij}^5+7a^2R_{ij}^3(21+kR_{ij})$$
$$+8ka^6(3+3kR_{ij}+k^2R_{ij}^2)-a^3R_{ij}^2(264+46kR_{ij}+5k^2R_{ij}^2)+2a^4R_{ij}(150+55kR_{ij}+15k^2R_{ij}^2+k^3R_{ij}^3)$$
$$-4a^5(36+24kR_{ij}+13k^2R_{ij}^2+2k^3R_{ij}^3)) - \frac{21e^{-2+R_{ij}/a}(a-R_{ij})^2E_i\left(\frac{(1+ka)(2a-R_{ij})}{a}\right)}{a^4R_{ij}^3}$$
$$+\frac{7e^{-2+R_{ij}/a}(2a-R_{ij})(3a^2-3aR_{ij}+R_{ij}^2)E_i\left(\frac{(1+ka)(2a-R_{ij})}{a}\right)}{a^5R_{ij}^3}$$
$$-\frac{e^{R_{ij}/a}(-3a^3+3a^2R_{ij}-2aR_{ij}^2+R_{ij}^3)E_i\left(-\frac{R_{ij}}{a}\right)}{a^5R_{ij}^3} + \frac{e^{R_{ij}/a}(-3a^3+3a^2R_{ij}-2aR_{ij}^2+R_{ij}^3)E_i\left(-\frac{(1+ka)R_{ij}}{a}\right)}{a^5R_{ij}^3}$$
$$+\frac{21e^{-2+R_{ij}/a}(a-R_{ij})^2E_i\left(2-\frac{R_{ij}}{a}\right)}{a^4R_{ij}^3} - \frac{7e^{-2+\frac{R_{ij}}{a}}(2a-R_{ij})(3a^2-3aR_{ij}+R_{ij}^2)E_i\left(2-\frac{R_{ij}}{a}\right)}{a^5R_{ij}^3}. \quad \text{(A7)}$$


[1] H. Thomas, G.E. Morfill, V. Demmel, J. Goree, B. Feuerbacher, and D. Mohlmann, Phys. Rev. Lett. **73**, 652 (1994).

[2] J.H. Chu, I. Lin, Phys. Rev. Lett. **72**, 4009 (1994).

[3] K. Takahashi, *et al.* Phys. Rev. E **58**, 7805 (1998).

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

[5] M.S. Murillo and M. Rosenberg, in *Physics of Dusty Plasmas: 7th Workshop*, edited by Mihaly Horanyi, AIP Conf. Proc. No. **446** (AIP, New York, 1998).

[6] U. Mohideen, *et al.*, Phys. Rev. Lett. **81**, 349 (1998).

[7] D.P. Resendes (unpublished).

[8] J. D. Jackson, *Classical Electrodynamics* 2nd ed. (Wiley, New York, 1975), p. 141.

[9] Landau and Lifshitz, *Statistical Physics* 2nd ed. (Pergamon, Oxford, 1977), p. 227.

[10] E.C. Whipple, T.G. Northrop, and D.A. Mendis, J. Geophys. Res. **90**, 7405 (1985).