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A semiempirical mass formula for spherical Coulomb crystals

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Abstract
In analogy to the Bethe–Weizsäcker formula for nuclei we establish a semiempirical mass formula for the energies of Coulomb crystals including Madelung, surface, compression and curvature energy terms. The surface tension and the incompressibility are extracted as well. The coefficients are fitted at data obtained from molecular dynamics calculations for spherically confined systems of charged particles with particle numbers up to about 100 000 under their mutual Coulomb repulsion and under constant radial focusing. The systems are cooled down until the excess energy stays constant up to 10^{-8}. For particle numbers below about 10 000, they settle in icosahedral structures whose faces are rounded off. At about 10 000 particles there is a transition to body centred cubic (bcc) crystals where particles are arranged in parallel layers. The icosahedra have lower surface energy but slightly higher Madelung energy of -0.8949, in contrast to the bcc crystals which have the lower Madelung energy of -0.8959 but essentially larger surface energy. The icosahedra are more compressible than the bcc crystals.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The gross properties of a leptodermous (thin skinned) system like a nucleus, a water drop, or a cluster can well be described by a macroscopic semiempirical mass formula like the Bethe–Weizsäcker formula; see [1, 2]. Its major constituents are the (negative) volume energy, which is the binding energy of the corresponding infinite matter, and the (positive) surface energy, the loss of binding due to missing neighbours in the surface. The latter is balanced by the Coulomb energy. Further refinements also account for the loss of binding due to even more missing neighbours in a curved surface which results in the (positive) curvature energy and a gain in binding due to the overall compression of the system, the (negative) compression energy. The leading term is proportional to the volume ($\propto N$), the Coulomb energy—for equal numbers of

protons and neutrons—is $\propto N^{5/3}$, the surface energy is proportional to the surface area ($\propto N^{2/3}$) and the curvature and compression energies are $\propto N^{1/3}$, where N is the number of particles in the system. Usually mass formulae are given as energy per particle, thus dividing all terms by N.

Coulomb crystals are ensembles of charged particles which are confined by a constant external harmonic radial focusing force and are cooled to very low temperature. Then they crystallize into certain structures depending on the number of particles. They have a rather sharp surface and, hence, are leptodermous systems as well. In this paper we employ this analogy and state a semiempirical mass formula for spherical Coulomb crystals. For zero temperature, this mass formula contains only one single control parameter, namely the number of particles. In addition, the Wigner–Seitz radius as the unit of length and the unit of energy—the Coulomb energy of two particles at a distance of the Wigner–Seitz radius—contains all information about the external focusing. The excess energy here plays the role of the binding energy, and the Madelung energy plays the role of the volume energy, i.e. the energy per particle of the corresponding infinite system gained by ordering the particles.

2. Spherical Coulomb crystals

The properties and thermodynamics of *infinite* Coulomb matter with a neutralizing background have been studied extensively, see e.g. the work on the one-component plasma (OCP). For original work see [3] and for recent studies see [4]. For an infinite plasma parameter, which is the ratio of the Coulomb energy of two particles $\epsilon_0 = q^2/a_{\mathrm{WS}}$ at a distance of the Wigner–Seitz radius $a_{\mathrm{WS}} = (3/4\pi n)^{1/3}$ to thermal energy per particle, $\Gamma = \epsilon_0/kT$, where n is the particle density and q is the charge or, equivalently, for zero temperature, the particles settle into the body centred cubic (bcc) lattice with a Madelung energy per particle of $\epsilon_{\mathrm{Mad}} = -0.895\,929\,255\,682$ gained by arrangement in a lattice as compared to the energy per particle of the equivalent homogeneous system [4]. The density, in turn, adjusts in the trap with harmonic frequency ω_0 to $n = 3m\omega_0^2/4\pi q^2$. Here the Madelung energy is defined in units of ϵ_0 and the unit of length will be a_{WS}. Since Coulomb *matter* does not exist, already in 1987 *finite* Coulomb crystals were generated, e.g. by laser cooled ions in traps [5]. For a review on this subject, see [6]. The properties of such finite Coulomb crystals, however, are still not completely understood. The first theoretical work [7] on finite Coulomb crystals was done about the same time and ten years ago [8] we performed studies by molecular dynamics (MD) with particle numbers $N \leqslant 5000$. There we concluded, on the basis of the lowest excess energy, that the structure of finite spherical Coulomb crystals is of the type of multilayered Mackay icosahedra [9] despite the fact that the lowest energy configuration of infinite Coulomb matter is of bcc type. Their faces, however, are rounded off by the long-range Coulomb energy. The five-fold symmetry of icosahedra is typical for small quasicrystalline systems (the reason why icosahedral crystals do not exist) because their overwhelming surface energy is smaller than the one of real crystalline systems with their six-fold symmetry.

Only a few points above $N = 5000$ were calculated recently, with 10 000 particles by Schiffer [10] and four systems with $N > 5000$ by the Totsuji group [11]. The results of the latter group already indicated that systems with large particle numbers settle into different structures. In the meantime the speed of computers and the availability of computer time has increased dramatically so that nowadays ensembles with up to $N = 100\,000$ particles can be treated easily, thus coming much closer to the asymptotic limit $N \to \infty$. In this paper we confirm our old finding for small particle numbers and, in addition, calculate the transition from finite crystals to infinite ones at $N \approx 10\,000$. Also, from the dependence of the excess energy and the maximum radius on the particle number we extract the surface, compression and curvature energy coefficients as well as the incompressibility and surface tension.

3. Molecular dynamics

The MD [12] follows closely [8]. Starting with either of the random, bcc, fcc, hcp, or cubic configurations in a sphere or with multilayer Mackay icosahedra, the equations of motion of the N particles are solved under constant radial focusing and under their mutual Coulomb interactions. The layered bcc and shell-type icosahedral starting systems were chosen for obvious reasons, namely because we anticipate that the final annealed systems will be of that kind. The results will show that each type remains of the same type because the high potential barrier between them cannot be overcome with reasonable computing time in the MD calculations. The fcc and hcp were chosen because their Madelung energies of $\epsilon_{\rm Mad}^{\rm fcc} = -0.895\,873\,615\,195$ and $\epsilon_{\rm Mad}^{\rm hcp} = -0.895\,838\,120\,459$ [4] are just slightly higher than the bcc one. For the Mackay icosahedra only systems with closed shell numbers:

$$N = (2M+1)(\tfrac{5}{3}M[M+1]+1), \tag{1}$$

where $M = 1, 2, \ldots$ [13], are calculated.

Random initial systems do not have closed shells. Therefore the initial particle numbers of such systems were also chosen at random. On the other hand, the particle numbers of all other initial systems used were chosen so that their maximum radius corresponds to a closed shell. As usual, numerical cooling is achieved by reducing the momenta in a controlled way. Initially, as in the computation of Lennard-Jones clusters [13], radial scaling is applied in order to accelerate convergence and the equations of motion of the N particles were then iterated until the excess energy stays constant up to 10^{-8}.

4. Mass formula for spherical Coulomb crystals

First we calculate the excess energy $\epsilon_{\rm ex} = \epsilon_{\rm total} - (9/10)N^{2/3}$ which is the total energy per particle minus that of the equivalent homogeneous system of radius $\overline{R}$, which follows from minimization with respect to $\overline{R} = N^{1/3}$ of the Coulomb and confining components:

$$\overline{\epsilon}_{\rm Coul} = \frac{3}{5}\frac{N}{\overline{R}}, \qquad \overline{\epsilon}_{\rm fcc} = \tfrac{3}{10}\overline{R}^2. \tag{2}$$

As in the liquid drop model of nuclei [1] this energy is then expanded in terms of the small quantity $N^{-1/3}$:

$$\epsilon_{\rm ex} = \epsilon_{\rm Mad} + a_{\rm surf}N^{-1/3} + [a_{\rm curv} - a_{\rm comp}]N^{-2/3}. \tag{3}$$

This yields the volume ($\propto N^0$), surface ($\propto N^{-1/3}$), curvature and compression ($\propto N^{-2/3}$) energies per particle, respectively. Note that the last term contains two terms, the positive curvature correction and a negative contribution from scaling due to compression and, thus, the total term proportional to $N^{-2/3}$ might be positive or negative. As was done in fitting the coefficients of the Bethe–Weizsäcker semiempirical mass formula for nuclei, here we also restrict ourselves to closed shell (magic) systems. Systems in between shells would have an additional microscopic so-called shell energy.

In figure 1 the resulting excess energies are shown as a function of $N^{-1/3}$. Depending on the starting conditions the systems also settle into different final structures which will be discussed in more detail in section 5: multilayer icosahedra (open circles), rounded off by the Coulomb force, have $\epsilon_{\rm Mad} = -0.8949$ and $a_{\rm surf} = 0.0362$ for all particle numbers. BCC systems (open and full squares), on the other hand, have two distinct Madelung and surface energies, $\epsilon_{\rm Mad} = -0.8947$ and $a_{\rm surf} = 0.363$ for $N < 5000$ and $\epsilon_{\rm Mad} = -0.895\,93$ and $a_{\rm surf} = 0.0582$ for $N > 5000$, thus indicating a transition to a different structure at the right arrow. Random systems (open diamonds) have about the same $a_{\rm surf}$ as bcc systems but are

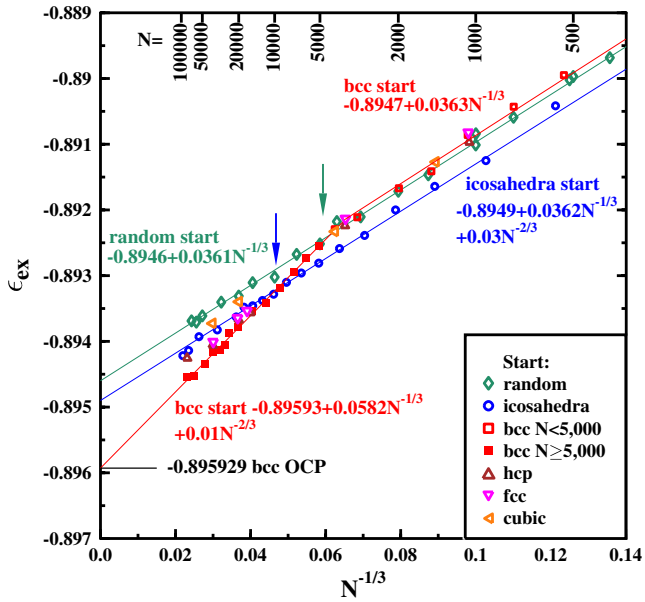

Figure 1. Excess energies of spherical Coulomb crystals from MD calculations. The arrows point to the particle numbers at transition.

slightly higher in energy due to the fact that the particle numbers never correspond to closed shells. The few cubic, fcc and hcp systems calculated (open triangles) settle into intermediate structures. The icosahedral line and the bcc line cross at the left arrow at $N \approx 10\,000$, when bcc systems become lower in energy. As a result, finite Coulomb crystals with $N < 10\,000$ always are of icosahedral type; at $N \approx 10\,000$ there is a phase transition to bcc structure with the correct Madelung energy of $\epsilon_{\mathrm{Mad}} = -0.895\,929$ of the infinite Coulomb matter indicated by the short line. This behaviour was expected because Itano *et al* [14] have already observed systems of $10^5 \ldots 10^6$ laser-cooled $^9\mathrm{Be}^+$ ions in a Penning with bcc structures.

The *rms* radii of the systems follow from simple geometrical considerations and must obey the relation [8]

$$R_{\mathrm{rms}} = \sqrt{\frac{3}{5}} N^{1/3} + \sqrt{\frac{5}{3}} \frac{\epsilon_{\mathrm{Mad}}}{3} N^{-1/3}. \tag{4}$$

This is well reproduced in figure 2. The *maximum* radii, however, also shown in figure 2,

$$R_{\mathrm{max}} = N^{1/3} - \tfrac{3}{5} - \mathcal{O}(N^{-1/3}), \tag{5}$$

contain additional information, namely the overall scaling by compression from the surface tension. The (negative) global scaling factor $-\overline{\delta} = -3/5$ in $R_{\mathrm{max}} = N^{1/3}(1 - \overline{\delta} N^{-1/3})$ also applies locally to all particle coordinates. According to the droplet model the incompressibility K is given by $K = 2a_{\mathrm{surf}}/\overline{\delta}$ from which follows the compression energy coefficient

$$a_{\mathrm{comp}} = 2a_{\mathrm{surf}}^2/K. \tag{6}$$

The compression energy is a gain, i.e. a negative contribution to the excess energy due to the favourable compression of the system. The term (6) has to be subtracted from the total contribution to the energy per particle proportional to $N^{-2/3}$ to yield the positive curvature energy correction. The surface *tension* τ is related to the surface *energy* through $\tau = a_{\mathrm{surf}}/4\pi a_{\mathrm{WS}}^2$ by virtue of its definition $E_{\mathrm{surf}} = \tau \times$ surface. The various quantities

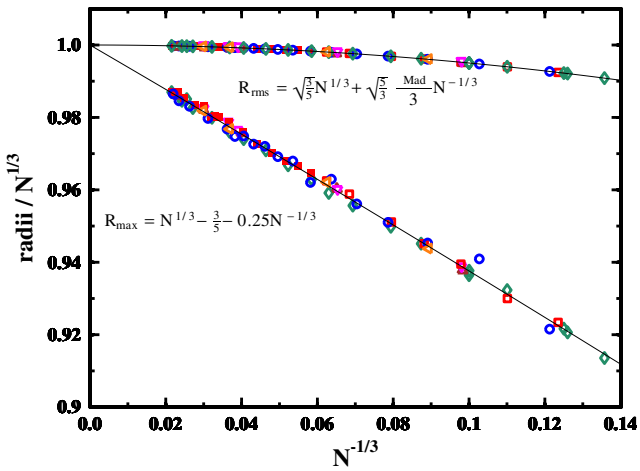

Figure 2. RMS radii and maximum radii. For clarity, the rms radii are divided by $\sqrt{3/5}$. Same key as in figure 1.

Table 1. Various quantities of finite Coulomb crystals compared to nuclear data. Energies are in units of ϵ_0 and radii are in units of a_{WS}. For nuclei, $a_0 = 1.2$ fm and $\epsilon_0 = 1.2$ MeV.

	Coulomb crystals		
	Icosahedra $N < 10\,000$	BCC $N > 10\,000$	Nuclei
Madelung (volume) energy, ϵ_{Mad}	-0.8949 ± 0.0001	$-0.895\,93$	-6.7
Surface energy coefficient, a_{surf}	0.036 ± 0.002	0.058 ± 0.002	15.4
Surface tension, τ	$0.0029 \pm 0.000\,02$	$0.0046 \pm 0.000\,02$	1.2
Scaling factor, $\overline{\delta}$	0.6 ± 0.01	0.6 ± 0.01	0.37
Incompressibility, K	0.12 ± 0.005	0.19 ± 0.005	80
Compression energy coeff., a_{comp}	0.022 ± 0.001	0.035 ± 0.001	5.8
Curvature energy coefficient, a_{curv}	0.032 ± 0.002	0.065 ± 0.002	10 ± 4

resulting from this analysis are listed in table 1 and are compared with the corresponding quantities for nuclei. For nuclei we employ as units the nuclear radius constant $r_0 = 1.2$ fm and $\epsilon_0 = e^2/r_0 = 1.2$ MeV. Here we note that, apart from the fact that the nuclear force is much stronger, Coulomb crystals are more compressible than nuclei and that the coefficients are of the same order of magnitude relative to each other.

5. Structures

Finally, we turn briefly to the discussion of the final structures of spherical Coulomb crystals with large numbers of particles. For this purpose we analyse the radial distribution function and the nearest neighbour radial and angular correlation functions. The icosahedral start configurations settle relatively fast into their final structures, thus indicating that there is little restructuring. Onion-like shells remain shells as has been analysed earlier for small systems, e.g. in [7]. Random starting configurations, on the other hand, due to their completely disarranged initial structures, need weeks of CPU time to settle. As can be seen from figure 3, where the radial distribution functions (divided by r^2) of two nearest neighbours are shown, all

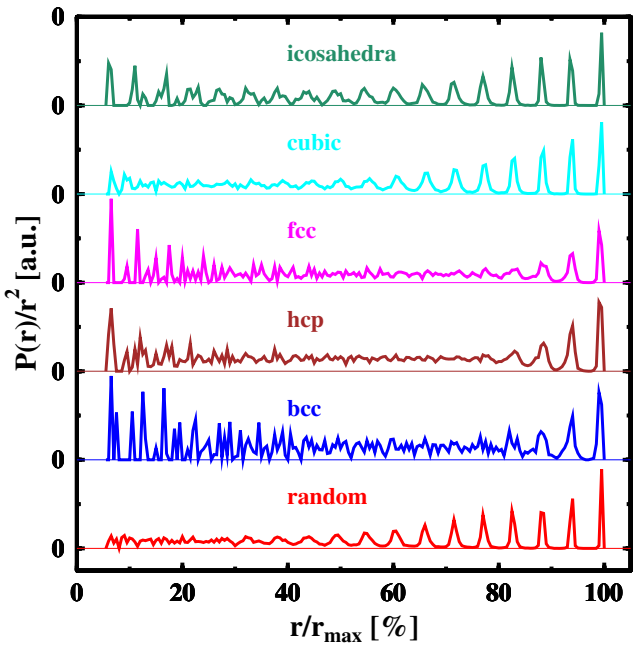

Figure 3. Radial distribution functions for various final structures with $N \approx 50\,000$.

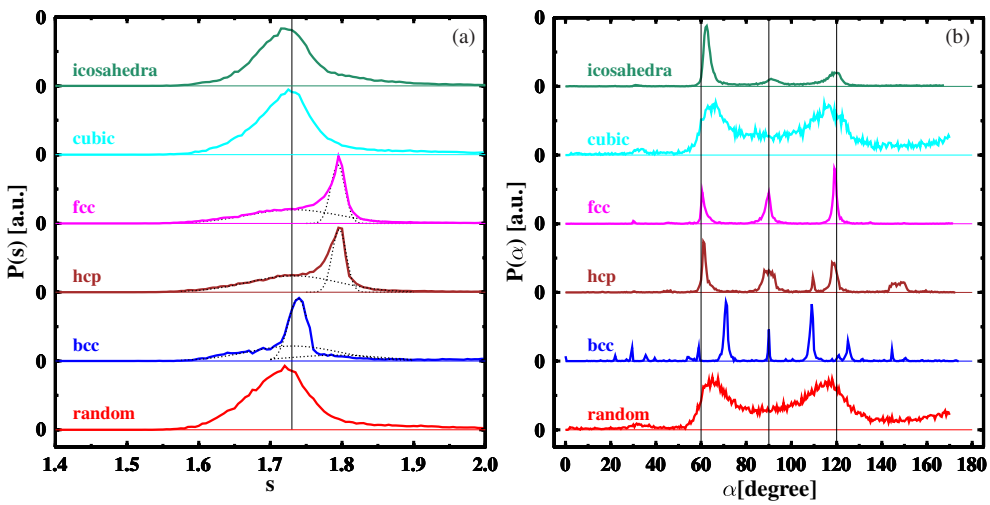

Figure 4. Nearest neighbour radial (a) and angular (b) correlation functions for various large final structures with $N \approx 50\,000$.

radial shells of the icosahedral configuration are very pronounced. This also, to some extent, applies to the random start configuration, i.e. this system tries to settle into radial shells. The interior shells, however, are still not completely pronounced. The bcc start configuration with its minimum energy, however, develops only about three to four radial shells just in the surface. The interior remains radially uncorrelated but consists of graphite-like plane layers as in the original bcc structure. FCC and hcp behave similarly whereas the cubic configuration also tries to settle into shells.

The radial correlation functions of two nearest neighbours shown in figure 4 peak about at $s = 1.7$ as in [8, 10]. For fcc, hcp and bcc, the correlations are well maintained even across the surfaces, which manifests itself in the fact that the subpeaks, indicated by the dotted curves, are resolved. The angular correlation functions of figure 4 resolve the bcc peaks at 70.5° and 109.5° and the peaks of the Mackay icosahedra at the weighted centre of 58.3°, 60° and 63.4°.

As found earlier [7, 8], all systems with particle numbers well below 5000 always settle into spherical shells regardless of their initial configuration.

6. Summary

In summary, in analogy to the droplet mass formula of leptodermous systems we have calculated and fitted the coefficients of the semiempirical mass formula for Coulomb crystals up to the order $N^{1/3}$, i.e. the Madelung, surface, curvature and compression energy coefficients and related quantities like surface tension, incompressibility and scaling factor. In [11] three systems with $N > 5000$ have been computed. Now, based on good statistics of more than 100 configurations, we have also shown that small spherical Coulomb crystals with particle numbers up to about 10 000 are arranged in more or less *spherical* shells whereas larger ones in the interior consist of *plane* layers and also have a few spherical shells in the surface. The latter have lower Madelung energy but higher surface energy than the former. The *rms* deviation of the energies from the fits of the semiempirical mass formula for both branches is $\langle \epsilon_{\text{total}} \rangle_{\text{rms}} = 3 \times 10^{-5}$.

Further work is in progress concerning extensions of the mass formula to include deformations and rotations and to analyses of the incompressibility and surface tension.

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