On the ground state of the one-component classical plasma

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Abstract. We consider the ν-dimensional one-component classical plasma model in a spherical domain. We give an heuristic derivation of the H-stability bounds which enables us to understand their physical meaning as well as the nature of the ground state. Then, accurate estimations of the binding energy of various Wigner lattices are found theoretically as well as computed numerically. For $\nu = 2$ dimensions, the lowest energy configuration of particles corresponds to the triangular lattice. For $\nu = 3$ dimensions, our results agree with those of Coldwell-Horsfall and Maradudin.

1. Introduction

The term 'plasma' denotes a gas of charged particles of opposite electrical charges possessing overall neutrality. The point charged particles (electrons) may be immersed in an uniform neutralizing background of positive charge and density ρ. This model of a plasma, which we shall treat classically, is then referred to as the one-component plasma (OCP). In any dimension ν, the thermodynamic state of this system is characterized essentially (Sari and Merlini 1975), by the dimensionless parameter $\gamma^{(\nu)} \equiv \beta e^2 \rho^{(\nu-2)/\nu}$, $(\beta = 1/kT)$.

As in other models of statistical mechanics, some different features, due to the dimensionality arise in this system, the Coulomb potential being defined as the fundamental solution of the Poisson equation. These differences appear, for example, in thermodynamics (equation of state).

It is only recently‖ that the existence of the thermodynamic limit of the free energy density possessing good convexity properties (in a certain region of $\gamma^{(\nu)}$), has been proved for $\nu > 1$ ($\nu = 3$ dimensions, Lieb and Narnhofer 1975; $\nu = 2$ dimensions, Sari and Merlini 1976). This existence is partially assured by the H-stability property which requires that there exists a lower bound (density dependent) to the potential energy per particle, $V^{(\nu)}(N) \geq -Nb^{(\nu)}(\rho)$, for any configuration of N particles in the box. From the mathematical point of view, such a bound provides a lower bound to the free energy density.

‖ The present work was done before these results were established.

However, it might be observed, although it can rarely be proved, that some many-body potentials reach their minima at regular lattice structures. Some years ago, Wigner (1938) had realized that at sufficiently low densities, the three-dimensional (OCP) model could crystallize into a solid—the so called *Wigner lattice*. This crystalline state, or phase, may be expected to exist not only in the ground state, but also at finite temperatures. A known example is given precisely by the classical OCP in one dimension: the state of lowest energy corresponds (Choquard and Sari 1973) to that of a crystal for which ρ^{-1} is the lattice constant and $-b^{(1)}(\rho) = e^2/12\rho$ the binding energy; at finite temperatures in the one-component model limit, a periodicity property of the correlation functions was discovered (Baxter 1964) in the associated eigenvalue problem. Afterwards, it was shown (Kunz 1974) that the system is indeed in a crystalline state for all temperatures and densities. This crystal is nothing else but the classical analogue of the Wigner lattice. More generally, for any ν, we shall see that the potential energy of the system contains a translationally invariant two-body contribution (the Coulomb potential), of repulsive type, and a one-body term (harmonic potential), due to the continuum which has the effect of attracting each particle to the centre of the box, taken to be spherical for the sake of simplicity. Thus, the existence of particle configurations which minimize the net electrostatic interaction energy ($V_{min}^{(\nu)}(N) \sim -\alpha N$), is not excluded *a priori* for $\nu > 1$.

Since Wigner's original work, there has been much effort devoted to the study of the solid phase of the OCP (Salpeter 1961, Coldwell-Horsfall and Maradudin 1960, Brush *et al* 1966, Pollock and Hansen 1973) in the three-dimensional case. The lattice with the lowest binding energy should, in all probability, be among one of the most symmetrical types, cubic centred, cubic face centred or hexagonal of 'close packed' type. Unfortunately, the energies of different lattices can be computed only with limited accuracy; and since the difference between them amounts to several percent only, the question of the choice of the most stable lattice remains unsolved. In the two-dimensional case, no result is known about this subject.

The purpose of this paper is twofold: to give an heuristic derivation of the H-stability bounds, as well as their physical interpretation, and to characterize the state of lowest energy of the system (§§ 2 and 3). The numerical values of the binding energy of various lattices ($\nu = 2$ and 3 dimensions) are obtained, (§ 4). The credibility of our numerical results is tested by a simple and accurate theoretical estimation of binding energies, which is derived in a controlled approximation.

2. The H-stability property

2.1. Definition of the model with impenetrable wall boundary conditions

We consider the classical OCP model in the ν-dimensional ball $B^{(\nu)}(R)$, of radius R and centred at the origin. The volume of $B^{(\nu)}(R)$ is given by $|B^{(\nu)}(R)| = S_\nu R^\nu \nu^{-1}$, where $S_\nu = 2\pi^{\nu/2}\Gamma(\nu/2)$ is the surface of the ν-dimensional unit sphere.

The N point charges (particle charge $-e$) are in the domain $B^{(\nu)}(R)$ in the presence of an inert and homogeneous neutralizing background of charge density $|e|\rho \equiv |e|N/|B^{(\nu)}(R)|$. We shall always assume overall charge neutrality for the system.

From electrostatics, the effect of the uniform background is that of an attractive one-body harmonic potential; and one suspects the existence of a *ground state*, i.e. a configuration X^0 of particles with minimum energy corresponding to the most stable arrangement of particles.

The potential energy of the system consists of three contributions:

$$V^{(\nu)}(N) = V_{pp}^{(\nu)} + V_{pb}^{(\nu)} + V_{bb}^{(\nu)}$$

$$= \frac{e^2}{2} \sum_{i \neq j}^{N} \phi^{(\nu)}(|x_i - x_j|) - e^2 \rho \sum_{i=1}^{N} \int_{B^{(\nu)}(R)} d^\nu x \, \phi^{(\nu)}(|x - x_i|)$$

$$+ \frac{e^2 \rho^2}{2} \iint_{(B^{(\nu)}(R))^2} d^\nu x \, d^\nu y \phi^{(\nu)}(|x - y|) \tag{2.1}$$

where the Coulomb interaction potential $\phi^{(\nu)}(|x|)$, defined by

$$\phi^{(\nu)}(|x|) = \begin{cases} \mathrm{sgn}(\nu - 2)|x|^{2-\nu} & \nu \neq 2 \\ \ln |x|^{-1} & \nu = 2 \end{cases} \tag{2.2}$$

is the fundamental solution (Wermer 1974), which at infinity vanishes for $\nu > 2$, and becomes infinite for $\nu = 1, 2$, of the ν-dimensional Poisson equation (Schwartz 1965)

and
$$\Delta \, \phi^{(\nu)}(|x|) = -|\nu - 2|S_\nu \, \delta_\nu(|x|) \qquad \nu \neq 2$$
$$\Delta \cdot \ln |x| = -2\pi \, \delta(|x|) \qquad \nu = 2.$$

With these definitions of $\phi^{(\nu)}(|x|)$ we can evaluate (2.1) and, after performing the integrations, we have the following explicit form for the total potential energy:

$$V^{(\nu)}(N) = \frac{e^2}{2} \sum_{i \neq j}^{N} \phi^{(\nu)}(|x_i - x_j|) + \frac{e^2 N}{2R^{\nu-2}} \sum_{i=1}^{N} \left(\frac{|x_i|}{R}\right)^2 - \tilde{B}_\nu(\nu, R, N), \tag{2.2}$$

where

$$\tilde{B}_\nu = \left(\frac{\nu + 1}{\nu + 2} + \phi^{(\nu)}(R)R^{\nu-2}\right)\frac{e^2 N^2}{2R^{\nu-2}}$$

Since $S_\nu R^\nu \rho = \nu N$, $\tilde{B}_\nu$ can also be written as

$$\tilde{B}_\nu = \begin{cases} \left[|\nu - 2|\left(\frac{\nu+1}{\nu+2}\right) + \mathrm{sgn}(\nu - 2)\right]\frac{e^2}{2}\left(\frac{\rho S_\nu}{\nu}\right)^{1-2/\nu} N^{1+2/\nu}, & \text{for } \nu \neq 2 \\[3mm] \left[\frac{\nu+1}{\nu+2} + \frac{1}{2}\ln\left(\frac{\rho S_\nu}{\nu N}\right)\right]\frac{e^2}{2}N^\nu, & \text{for } \nu = 2. \end{cases}$$

For $\nu = 1$, the particles can be naturally ordered, and our Hamiltonian coincides with the usual expressions (Baxter 1963, Choquard and Sari 1973). For $\nu = 2$, we obtain explicitly:

$$V^{(2)} = -\frac{e^2}{2} \sum_{i \neq j}^{N} \ln\left(\frac{|x_i - x_j|}{R}\right) + \frac{e^2 N}{2} \sum_{i=1}^{N} \left(\frac{|x_i|}{R}\right)^2 - \left(\frac{3N^2}{8} + \frac{N}{4}\ln\frac{\pi\rho}{N}\right)e^2.$$

The singular feature of the two-dimensional case is that the coordinates x_i only enter in the combination $|x_i|/R$ in the Hamiltonian, which is the essence of the scaling trick considered by various authors (Salzberg and Prager 1963, Knorr 1968, Hauge and Hemmer 1971, Deutsch and Lavaud 1974). However, in any dimension, there is the appearance of the one-body harmonic potential due to the presence of the background. Moreover, although the correlation functions may not be affected by the term $\tilde{B}_\nu$ which cancels out, the same is not true for the free energy, since it depends on the density and the dimensionality.

2.2. Lower bounds on $V^{(\nu)}(N)$

The first parameter which enters in the potential energy is the particle density ρ which, because of charge neutrality, coincides with that of the background. On the other hand, the second parameter, the dimensionality ν, enters, in particular, through the explicit dependence of the term $\tilde{B}_\nu$. Thus, the lower bounds for the energy will depend only on ρ and ν.

The lower bounds to the potential energy per particle can be found in the following way.

For a particle ($N = 1$) in the domain $B^{(\nu)}(R)$, the ground state corresponds to the configuration where this particle is at the centre of the domain. This is the configuration of highest symmetry. Then, for $N = 1$, we have for the energy of the ground state:

$$V^{(\nu)}(N=1) \equiv -b_{(\rho)}^{(\nu)} = \begin{cases} -\left[|\nu - 2|\left(\dfrac{\nu+1}{\nu+2}\right) + \mathrm{sgn}(\nu - 2)\right]\dfrac{e^2}{2}\left(\dfrac{\rho S_\nu}{\nu}\right)^{1-2/\nu}, & \text{for } \nu \neq 2 \\[4mm] -\left[\dfrac{\nu+1}{\nu+2} + \dfrac{1}{2}\ln\left(\dfrac{\rho S_\nu}{\nu}\right)\right]\dfrac{e^2}{2}, & \text{for } \nu = 2. \end{cases} \quad (2.3)$$

Adding other particles and increasing the domain $B^{(\nu)}(R)$, while keeping the density ρ constant, the energy per particle can only be greater, because of the Coulomb repulsion between the particles; and the symmetry of the configuration of particles can only be lower. Thus, the energy per particle for a particle ($N = 1$) in the ground state should be a lower bound to the energy per particle for $N > 1$. This can easily be verified for small N. Therefore, we propose the following bounds:

$$V^{(\nu)}(N) \geq -N b^{(\nu)}(\rho) \quad (2.4)$$

where the equality can eventually be approached very closely for the ground state of the system in the thermodynamic limit (see § 3).

Explicitly, we have:

$$b^{(1)}(\rho) = -e^2/12\rho$$
$$b^{(2)}(\rho) = e^2(\tfrac{3}{8} + \tfrac{1}{4}\ln \pi\rho) \quad (2.5)$$
$$b^{(3)}(\rho) = \frac{9e^2}{10}\left(\frac{4\pi\rho}{3}\right)^{1/3}$$

It is interesting to notice that the proposed bounds (2.5) are the exact ones, proved for $\nu = 1$ dimension by direct computation (Choquard and Sari 1973), for $\nu = 3$ dimensions (Lieb and Narnhofer 1974) and $\nu = 2$ dimensions (Sari and Merlini 1975) by using an idea due to Onsager (1933) where one replaces the point charges by smeared charge distributions.

However, the argument used in our heuristic derivation gives, for any dimension, the meaning of these lower bounds:—$b^{(\nu)}(\rho)$ is simply the Coulomb energy of the neutral elementary system (consisting of just one particle and the background) in the configuration of lowest energy.

3. Characterization of the ground state

In this section we analyse in more detail the lower bounds to the energy per particle and the nature of the state of the system of lowest energy (ground state). For the classical

OCP, this state is certainly obtained when the particles are at rest in the corresponding configuration X^0. This configuration defines the most stable arrangement of the particles.

The ground state is characterized, for instance, by the following properties.

Property 1. For $\nu \neq 1$, the configuration X^0 is infinitely degenerate.

This is due to the rotation invariance of the potential energy.

Property 2 (Peierls 1955). X^0 is an equilibrium configuration, i.e. the force on each particle i, $(i = 1, \ldots, N)$, vanishes:

$$\partial V^{(\nu)}(N)/\partial x_i = 0, \qquad \text{for } x_i \in X^0.$$

As Peierls remarked, this property is automatically satisfied for any arrangement of the particles in which the positions of each of them is a centre of symmetry of X^0 (infinite system). However, for a spherical box, the centre is the only centre of symmetry.

Property 3. For $x_i \in X^0$, necessarily we have $\Sigma_{i=1}^N x_i = 0$.

This condition expresses the fact that the centre of mass of particles is frozen at the origin or, in other words, that the dipole moment of the system vanishes.

Property 4. Let $\mathscr{L} \equiv \{(x_i)\}$ be the set of all possible configurations (x_i) of the system. For any $(x_i) \in \mathscr{L}$, we define a mapping $\chi : \mathscr{L} \rightarrow \mathscr{L}$, $x_i \rightsquigarrow \lambda x_i$, such that each vector x_i is dilated or retracted by λ ($\lambda \in \mathbb{R}^+$). Then, for any (x_i), the class $(\lambda x_i) \in \mathscr{L}$ possesses an element $(x_i') \equiv (\lambda_0 x_i)$ for which $V^{(\nu)}(N)$ is minimum.

In fact, if we write for the configuration (x_i) of particles $(V^{(\nu)}(N) \equiv V^{(\nu)}(N; x_i))$; $V_{pp}^{(\nu)} \equiv V_{pp}^{(\nu)}(x_i))$:

$$V^{(\nu)}(N; x_i) = V_{pp}^{(\nu)}(x_i) + A^{(\nu)}(x_i) - \tilde{B}_\nu$$

where $A^{(\nu)}(x_i) \equiv (e^2 N/2R^\nu) \Sigma_{i=1}^N |x_i|^2$, the condition $\partial V^{(\nu)}(N; \lambda x_i)/\partial \lambda = 0$ is equivalent to:

$$
\begin{aligned}
V_{pp}^{(\nu)}(\lambda x_i) &= 2A^{(\nu)}(\lambda x_i), && \text{for } \nu \neq 2 \\
e^2 N(N-1)/2 &= 2A^{(2)}(\lambda x_i), && \text{for } \nu = 2.
\end{aligned}
\tag{3.1}
$$

Let λ_0 be the value of λ for which the condition (3.1) is realized. One can verify that $\partial^2 V^{(\nu)}(N; \lambda x_i)/\partial \lambda^2 > 0$ for $\lambda = \lambda_0$. Hence, at the minimum of $V^{(\nu)}(N)$, that is for the configuration X^0 of particles, in any dimension:

$$V_{min}^{(\nu)}(N) = \tfrac{1}{2}\nu V_{pp}^{(\nu)} + \tfrac{1}{4} e^2 N(N-1) \delta_{\nu,2} - \tilde{B}_\nu \tag{3.2}$$

$\delta_{\nu,2}$ being the Kronecker symbol. From property 2, we deduce, for X^0, that λ_0 is normalized to unity, i.e. $V_{pp}^{(\nu)}(x_i) = 2A^{(\nu)}(x_i)$ for $x_i \in X^0$ and $\nu \neq 2$. Evidently, the mapping χ must be such that for the configuration (x_i) of particles in the ball $B^{(\nu)}(R)$, $\lambda_0 |x_i|$ is less than or equal to R to preserve the charge neutrality. Indeed, one can verify this for small N in any dimension. We assume that this holds for any N.

On the other hand, an easy manipulation yields:

$$
V_{bb}^{(\nu)} =
\begin{cases}
\left(\dfrac{\nu - 2}{2(\nu + 2)} + \dfrac{1}{2}\,\text{sgn}(\nu - 2) \right) \dfrac{e^2 N^2}{R^{\nu-2}}, & \text{for } \nu \neq 2 \\[3mm]
(\tfrac{1}{8} - \tfrac{1}{2} \ln R)\, e^2 N^2, & \text{for } \nu = 2
\end{cases}
$$

so that we have the following identity:

$$\tilde{B}_\nu \equiv \tfrac{1}{2}\nu V_{bb}^{(\nu)} + \tfrac{1}{4} e^2 N^2 \, \delta_{\nu,2}.$$

Consequently, the equality (3.2) reads:

$$V_{min}^{(\nu)}(N) = \tfrac{1}{2}\nu(V_{pp}^{(\nu)} - V_{bb}^{(\nu)}) - \tfrac{1}{4} e^2 N \, \delta_{\nu,2}. \tag{3.3}$$

The purpose is now to simplify further the right-hand side of the relation (3.3), thus giving another method, albeit intuitive, to establish the validity of the bounds (2.5) we established in § 2.

For the configuration X^0 of particles, let us decompose the domain $B^{(\nu)}(R)$ into N cells Δ_i (Δ_i containing x_i, $x_i \in X^0$), such that $|\Delta_i|\rho = 1$, with $\bigcup_{i=1}^{N} \Delta_i \equiv B^{(\nu)}(R)$ and $\Delta_i \cap \Delta_j = \phi(i \neq j)$. The domains Δ_i do not overlap; and the set $\{\Delta_i, \ i = 1, \ldots, N\}$ constitutes a subdivision of $B^{(\nu)}(R)$. Then, by definition:

$$V_{bb}^{(\nu)} = V_C^{(\nu)} + \sum_{i=1}^{N} V^{(\nu)}(\Delta_i)$$

where $V_{bb}^{(\nu)}$ is the self-energy of the ball $B^{(\nu)}(R)$, $V_C^{(\nu)}$ is the Coulomb interaction between the cells Δ_i, and $V^{(\nu)}(\Delta_i)$ is the self-energy of the cell Δ_i.

Then the relation (3.3) reads:

$$V_{min}^{(\nu)}(N) = \tfrac{1}{2}\nu(V_{pp}^{(\nu)} - V_C^{(\nu)} + V_C^{(\nu)}) - \tfrac{1}{2}\nu V_{bb}^{(\nu)} - \tfrac{1}{4} e^2 N \, \delta_{\nu,2}$$

$$= \tfrac{1}{2}\nu(V_{pp}^{(\nu)} - V_C^{(\nu)}) - \tfrac{1}{2}\nu \sum_{i=1}^{N} V^{(\nu)}(\Delta_i) - \tfrac{1}{4} e^2 N \, \delta_{\nu,2}. \tag{3.4}$$

Neglecting the terms $\tfrac{1}{2}\nu(V_{pp}^{(\nu)} - V_C^{(\nu)})$, we see that:

$$V_{min}^{(\nu)}(N) \gtrless -N(\tfrac{1}{2}\nu V^{(\nu)}(\Delta_0) + \tfrac{1}{4} e^2 \, \delta_{\nu,2}) \equiv -Nb^{(\nu)}(\rho)$$

where Δ_0 is the neutral ball $B^{(\nu)}(R)$ containing one point charge. The last inequality gives a new interpretation of the H-stability bounds—$b^{(\nu)}(\rho)$ in terms of the self-energy of Δ_0. These lower bounds are absolute minima of $V^{(\nu)}(N)$ for all N and all domains, since (as one can show by isoperimetric inequalities), the self-energy of a ball is always greater than that of any other cell of the same volume. Notice that for $\nu = 1$ dimension, $V_{pp}^{(1)} = V_C^{(1)}$ in (3.4).

Up to now, we have not been able to prove (for $\nu > 1$) that the configuration of particles with minimum energy has a crystalline structure. Assuming that for a very large system ($N \gg 1$) the energy minimum is reached for a crystalline configuration of particles, and under the hypothesis of a crystal without distortion, all the cells have the same lattice constant; then they correspond to Wigner–Seitz cells, Δ_{WS} (also called Voronoï polyhedra or Dirichlet regions). Of course boundary effects are not taken into account (the fact that for particles at the boundary, the associated dual cells are not strictly Wigner–Seitz cells) in the limit of an infinite system, these effects vanish. Neglecting $(V_{pp}^{(\nu)} - V_C^{(\nu)})$ in (3.4) (this contribution comes from a very short-ranged potential for the crystalline configurations we consider), we obtain our zeroth-order approximation of the binding energy per particle of two- and three-dimensional Wigner lattices:

$$\lim_{\substack{N\to\infty \\ R\to\infty \\ \rho \text{ fixed}}} \left(\frac{V_{lattice}^{(\nu)}(N)}{N} \right)_0 \equiv v_{lattice}^{(\nu)} \cong -\tfrac{1}{2}\nu V^{(\nu)}(\Delta_{WS}) - \tfrac{1}{4} e^2 \, \delta_{\nu,2}. \tag{3.5}$$

Our estimation (3.5) gives a surprisingly accurate value for the energy of lattices in any dimension ν. Comparison with numerical results will be presented in the next section. Moreover, the correctness of all the hypotheses involved previously in our analysis will be confirmed numerically.

4. The energy of Wigner lattices

This section is devoted first to the results of the numerical analysis which was carried out on systems up to $N \sim 6000$ particles in $\nu = 2$ and 3 dimensions, for the two-dimensional hexagonal, square and triangular lattices and the simple cubic lattice. In this analysis, the potential energy per particle has been plotted as a function of the number of particles in the various cases. Using the results of § 3, we have obtained the zeroth-order approximation of the binding energy for various structures and compared these values with the numerical results deduced from the energy curves, the bounds of the H-stability (2.5), and moreover for $\nu = 3$ with the known values for cubic lattices (Coldwell–Horsfall and Maradudin 1960). In both cases, $\nu = 2$ and 3 dimensions, our estimation (3.5) gives very satisfactory results for each crystalline configuration. In the following formulae, we have put the electron charge equal to -1.

4.1. The two-dimensional case

First, we have calculated by computer the lattice constant $a(N)$, $|z|_{\max}$ the maximum of $|z_i| \equiv |x_i|/R$, and the reduced quantity:

$$u^{*(2)}(N) \equiv \frac{V^{(2)}(N) + N b^{(2)}(\rho)}{N}$$

$$= \frac{N-1}{4}\left[\ln\left(\frac{1}{\gamma^2(N)}\right) - \frac{1}{2}\right] + \frac{1}{4}\ln N - \frac{1}{2N}\alpha(N)$$

where $(\gamma^2(N))^{-1} \equiv 2\,\Sigma_{i=1}^{N}\,|x_i|^2/(N-1)$ and $-\alpha(N)/2$ is the total Coulomb energy of N particles on a lattice with the lattice constant equal to 1. Plots of $u^{*(2)}(N)$ are given in figures 1, 2 and 3 for the triangular, square and hexagonal lattices. We have observed that, for the crystalline configuration with the minimum energy, $|z|_{\max}$ approaches asymptotically quickly the value 1. Thus the corresponding crystalline configuration grows with the number of particles N and the volume of $B^{(2)}(R)$ (the density ρ fixed), so that it covers the whole domain. Of course, 'small' oscillations of $u^{*(2)}(N)$, due to the sensitivity of the system to the symmetry of the ordered structure for finite N, are observed.

  Then, in each case, the integral of the self-energy of the Wigner–Seitz cell Δ_{WS}, with the lattice constant equal to 1, has been computed numerically. The results are:

$$C_{\mathrm{WS}}^{(2)} \equiv \int\!\!\int_{(\Delta_{\mathrm{WS}})^2} \mathrm{d}^2 x\,\mathrm{d}^2 y\,\ln|x-y| = \begin{cases} -2{\cdot}307165 & \mathrm{WS} \equiv \overset{1}{\diamondsuit} \\ -0{\cdot}805123 & \mathrm{WS} \equiv \overset{1}{\square} \\ -0{\cdot}220594 & \mathrm{WS} \equiv \triangle^1. \end{cases} \tag{4.1}$$

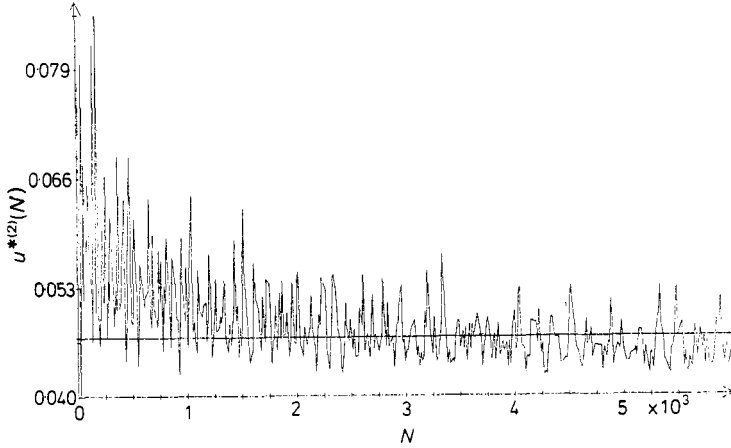From the formula (3.5), we obtain for the zeroth-order approximation of the binding

Figure 1. Plot of $u^{*(2)}(N)$ for the hexagonal lattice. The H-stability bound corresponds to $u^{*(2)}(N) = 0$. The horizontal line represents the mean value $\overline{u^{*(2)}}$ up to $N = 5750$ (table 1).
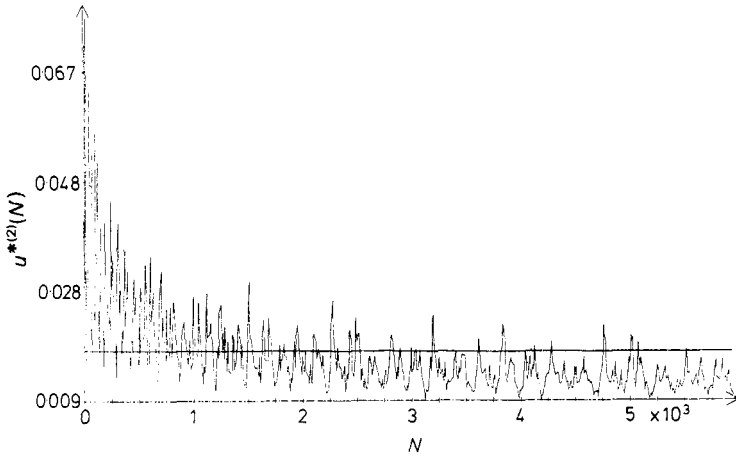

Figure 2. Plot of $u^{*(2)}(N)$ for the square lattice. The H-stability bound corresponds to $u^{*(2)}(N) = 0$. The horizontal line is the same as for figure 1.

energy per particle of the three two-dimensional lattices:

$$v^{(2)}_{\text{lattice}} = \tfrac{1}{2}\rho^2 \int\!\!\int_{\text{(WS)}^2} d^2x\, d^2y\, \ln|x-y| - \tfrac{1}{4}$$

$$= -b^{(2)}(\rho) + \begin{cases} \tfrac{1}{8}\ln(4\pi^2 e/27) + \tfrac{2}{27}C^2_{\text{hex}} & \text{for the hexagonal lattice} \\[4pt] \tfrac{1}{8}\ln(\pi^2 e) + \tfrac{1}{2}C^{(2)}_{\text{squ}} & \text{for the square lattice} \\[4pt] \tfrac{1}{8}\ln(16\pi^2 e/3) + \tfrac{8}{3}C^{(2)}_{\text{tri}} & \text{for the triangular lattice.} \end{cases} \tag{4.2}$$

A comparison of our theoretical estimations (4.2) of the binding energy per particle of the three lattices with numerical asymptotic limits of $u^{*(2)}(N)$ to be defined below, is given in table 1.
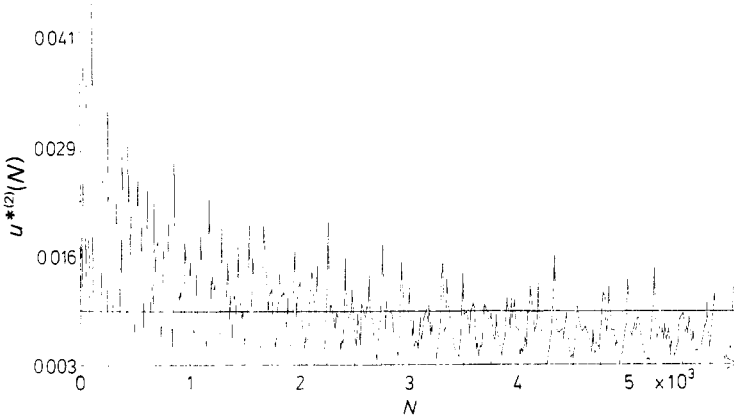
Figure 3. Plot of $u^{*(2)}(N)$ for the triangular lattice. The H-stability bound corresponds to $u^{*(2)}(N) = 0$. The horizontal line is the same as for figure 1.

Table 1. Comparison of the numerical results (asymptotic limit of the energy curves) and the theoretical estimations (equation 4.2).

Lattices	Numerical results	Theoretical estimations
Hexagonal	$-b^{(2)}(\rho) + 0.04678$	$-b^{(2)}(\rho) + 0.032170$
Square	$-b^{(2)}(\rho) + 0.01723$	$-b^{(2)}(\rho) + 0.008628$
Triangular	$-b^{(2)}(\rho) + 0.01067$	$-b^{(2)}(\rho) + 0.001588$

We remark that for the square lattice, the self-energy of the Wigner–Seitz cell (unit volume) can be computed exactly. Thus:

$$v_{squ}^{(2)} = \tfrac{1}{2}\rho^2 \int\int_{(\square)^2} d^2x \, d^2y \, \ln|x - y| - \tfrac{1}{4}$$

$$= -\tfrac{1}{4}(-\ln \rho + \tfrac{2}{3}(\pi + \ln 2) - \tfrac{25}{4}) - \tfrac{1}{4}$$

$$= -b^{(2)}(\rho) + \tfrac{1}{4}(\ln \pi + \tfrac{2}{3}(\pi + \ln 2) - \tfrac{11}{3})$$

$$= -b^{(2)}(\rho) + 0.008639$$

which agrees with the value given in table 1.

In conclusion, our zeroth-order approximation, $v_{lattice}^{(2)}$, (equation (4.2)), agrees very well with the numerical results and indicates clearly that the triangular lattice has the lowest energy.

4.2. The three-dimensional case

From our numerical analysis ($N \sim 6000$ particles), there is no indication that the energy of the FCC lattice is greater than that of the BCC lattice. Moreover, the corresponding known values (Coldwell-Horsfall and Maradudin 1960), coincide up to the third decimal; this will be reported elsewhere.

Using a computer, we have calculated the energy levels with the help of the formula:

$$\frac{V^{(3)}_{\min}(N)}{N} = -\frac{9}{10}\left(\frac{4\pi\rho}{3}\right)^{1/3}\left[\frac{5}{3N} V_{PP}^{2/3}\left(\sum_{i=1}^{N} |x_i|^2\right)^{1/3} - N^{2/3}\right]$$

$$\equiv -\frac{9}{10}\left(\frac{4\pi\rho}{3}\right)^{1/3} u^{*(3)}(N),$$

$-\frac{9}{10}(4\pi\rho/3)^{1/3}$ being the absolute minimum of $V^{(3)}(N)/N$. Notice that $u^{*(3)}(N)$ is independent of the choice of the lattice constant; and we expect that the value of $u^{*(3)}(N)$ is near to unity for large N. The function $u^{*(3)}(N)$ is plotted in figure 4 for the simple cubic lattice only.
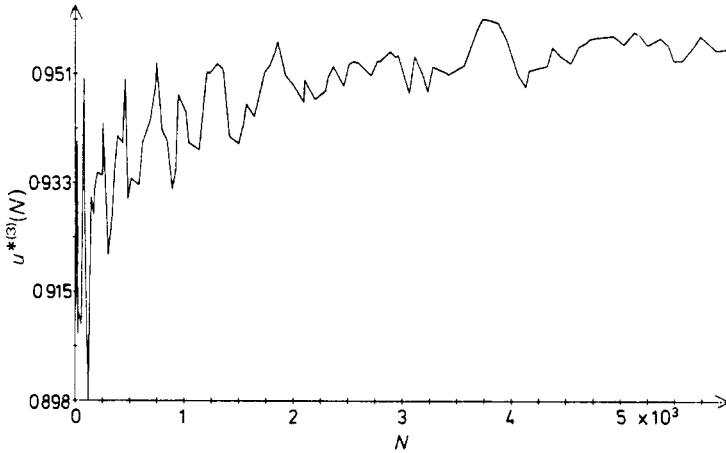

Figure 4. Plot of $u^{*(3)}(N)$ for the simple cubic lattice. The H-stability bound corresponds to $u^{*(3)}(N)$ equal to one.

On the other hand, as for $\nu = 2$ dimensions, our zeroth-order approximation for the binding energy of the cubic lattices has been obtained from formula (3.5). Let $C_{WS}^{(3)}$ be the quantity defined by:

$$C_{WS}^{(3)} \equiv \int\int_{(\Delta_{WS})^2} \frac{d^3x \, d^3y}{|x - y|}.$$

The volume of the Wigner–Seitz cell is chosen to be equal to 1 for the SC lattice, 2 for the FCC lattice and 4 for the BCC lattice. The nearest-neighbour distance is equal to 1 for the SC lattice, $2^{1/6} = 1 \cdot 12$ for the FCC lattice and $\sqrt{3}(4)^{-1/3} = 1 \cdot 09$ for the BCC lattice. The value of $C_{WS}^{(3)}$ has been computed numerically for the various cases. The results are:

$$C_{WS}^{(3)} = \begin{cases} 1 \cdot 88231 & \text{for SC (WS)} \\ 6 \cdot 09245 & \text{for FCC (WS)} \\ 19 \cdot 35494 & \text{for BCC (WS)}. \end{cases} \tag{4.3}$$

In table 2, we compare the numerical results taken from the energy curves $u^{*(3)}(N)$, the values of our zeroth-order approximation and those given by Coldwell-Horsfall and Maradudin.

Table 2. Comparison of the numerical results (asymptotic limits of the energy curves), the theoretical estimations (equation (3.5)) and the values of Coldwell-Horsfall and Maradudin (C-HM) for the cubic lattices ($\epsilon \equiv (4\pi\rho/3)^{1/3}$).

Lattices	Numerical	Theoretical estimations	C-HM values
SC	$\sim 0.85\epsilon$	-0.875770ϵ	-0.8806ϵ
FCC	—	-0.892840ϵ	-0.8953ϵ
BCC	—	-0.893422ϵ	-0.8958ϵ

We remark that, as for the square lattice ($\nu = 2$ dimensions), the self-energy of the Wigner–Seitz cell (unit volume) of the simple cubic lattice can be calculated exactly. Thus

$$C_{SC}^{(3)} = 4 \ln\left(\frac{1+\sqrt{3}}{\sqrt{2}}\right) - \frac{2\pi}{3} - \frac{4\sqrt{3}}{5} + \frac{2\sqrt{2}}{5} + 2 \ln(1+\sqrt{2}) + \frac{2}{5}$$

$$= 1.882312645$$

which coincides with the value obtained by computer and given in (4.3).

We make the following remarks.

(i) It must be mentioned that the sequence of particles, i.e. the arrangement and the different values of N for each lattice structure, has been chosen as such for simplicity; that is in such a way that for all N the arrangement of particles exactly fills a certain number of shells around the origin and does this without distortion. Thus there is no screening here; we compute the lattice constant $a(N)$ for each sequence of particles in the corresponding crystalline configuration, verify that all the particles are in the spherical domain (and in fact cover the whole spherical domain) and compute the Coulomb energy per particle; the lattice constant $a(N)$ varies at each step and is a function of N. This contrasts with the usual method in which, from the beginning, the particles are considered on an infinite lattice.

(ii) For $\nu = 3$ the numerical computation for the simple cubic lattice has been given for illustration; no extrapolation to infinite N is made in this work; moreover, the computations indicate that for a finite lattice ($N \sim 6000$) the energy per particle is 2% above the limiting energy of Coldwell-Horsfall and Maradudin and of our theoretical zeroth-order estimation for the infinite lattice.

(iii) For $\nu = 2$ the exact Madelung energy is not known up to date and a detailed theoretical analysis (the high-order correction to our zeroth-order estimation in this paper), which gives the energy exactly up to 10^{-6} for $u^{*(2)}(N)$, will be given elsewhere (Sari, Merlini and Calinon, in preparation). Moreover, an extrapolation method of the numerical analysis presented in this work will also be given in detail, as well as a comparison with the exact Madelung energy.

(iv) A crude 'asymptotic' value of $u^{*(2)}(N)$ or better, a mean numerical value has been calculated up to $N \sim 6000$. That is

$$\overline{u^{*(2)}} = \sum_{N=1}^{M} u^{*(2)}(N)/M$$

where M is the number of shells corresponding to $N = 5750$ (see figures 1, 2 and 3).

The numerical values are:

hexagonal lattice $\overline{u^{*(2)}} = 0 \cdot 04678$

square lattice $\overline{u^{*(2)}} = 0 \cdot 01723$

triangular lattice $\overline{u^{*(2)}} = 0 \cdot 01057.$

From the energy curves, we see that these values ($\nu = 2$) should only constitute an upper bound to the exact Madelung energy. Moreover, they are not too far from our zeroth-order theoretical estimation. This analysis also suggests that the triangular lattice should be the ground state of the two-dimensional one-component plasma.

5. Conclusions

Contrary to the two-dimensional case for the square and triangular lattices, the discrepancy between the energies of the FCC and the BCC lattices is insignificant. The fact that the BCC structure, which is not the most compact, is preferred to the FCC structure may be viewed as a very delicate balance of energy in the different spatial arrangements of particles. On the other hand, Wigner's approximation in which the polyhedral lattice cell is replaced by the Wigner–Seitz sphere is in error only by a multiplicative factor of $1 \cdot 00454$ for the BCC structure.

However, our estimation (3.5) of the total electrostatic interaction energy per particle agrees very well in any dimension and for different lattice structures with the numerical results obtained from our energy curves. The most attractive feature of the scheme which then emerges is that for the most part the work of calculating the binding energies consists of the computation of a 'geometrical structure constant'

$$\int\int_{(\Delta_{\mathrm{WS}})^2} \mathrm{d}^\nu x \, \mathrm{d}^\nu y \phi^{(\nu)}(|x-y|),$$

which must be calculated once and for all for each type of structure. It should be emphasized again that our treatment is not equivalent to the spherical approximation of Wigner and Seitz in which the polyhedron is approximated by a sphere. In fact, our method takes the actual shape of the polyhedron exactly into account. On the other hand, since we work to zeroth-order, we have neglected $(V_{\mathrm{pp}}^{(\nu)} - V_{\mathrm{C}}^{(\nu)})$, and since for large distances each term of $(V_{\mathrm{pp}}^{(\nu)} - V_{\mathrm{C}}^{(\nu)}) \simeq 0$, the higher-order approximations which take into account the clusters of neighbouring Wigner–Seitz cells would provide a better estimation of the binding energies.

Finally we must mention that for $\nu = 3$ dimensions, our zeroth-order approximation provides an upper bound on the energy levels. It should be useful to prove it. If it is true, then ($|\Delta_{\mathrm{sphere}}| \equiv |\Delta_{\mathrm{WS}}| = 1/\rho$):

$$-\frac{3}{2}\frac{\rho^2 e^2}{2}\int\int_{(\Delta_{\mathrm{sphere}})^2}\frac{\mathrm{d}^3 x \, \mathrm{d}^3 y}{|x-y|} < \lim_{N\to\infty}\left(\frac{V^{(3)}(N)}{N}\right)_{\mathrm{lattice}} < -\frac{3}{2}\frac{\rho^2 e^2}{2}\int\int_{(\Delta_{\mathrm{WS}})^2}\frac{\mathrm{d}^3 x \, \mathrm{d}^3 y}{|x-y|}.$$

It should also be interesting to prove that the energy of ionic crystals is again an upper bound to the binding energy of the OCP lattices. This last fact is observed, for example, in the simple cubic lattice of the OCP and in the caesium chloride structure which crystallizes on the cubic body centred structure.

Acknowledgments

References

Baxter R J 1963 *Proc. Camb. Phil. Soc.* **59** 779–87
—— 1964 *Phys. Fluids* **7** 38–43
Brush S G, Sahlin H C and Teller E 1966 *J. Chem. Phys.* **45** 2102–18
Choquard Ph and Sari R R 1973 *Helv. Phys. Acta* **46** 464–7
Deutsch C and Lavaud M 1974 *Phys. Rev.* A **9** 2595–616
Coldwell-Horsfall R A and Maradudin A A 1960 *J. Math. Phys.* **1** 395
Hauge E H and Hemmer P C 1971 *Phys. Norvegia* **5** 209–17
Knorr C 1968 *Phys. Lett.* **28A** 166–7
Kunz H 1974 *Ann. Phys. NY* **85** 303–35
Lieb E H and Narnhofer H 1975 *J. Stat. Phys.* **12** 291–309
Onsager L 1933 *J. Phys. Chem.* **43** 189–96
Peierls R E 1955 *Quantum Theory of Solids* (London: Oxford University Press)
Pollock E and Hansen J P 1973 *Phys. Rev.* A **8** 3110
Salzberg A and Prager S 1963 *J. Chem. Phys.* **38** 2587
Salpeter E E 1961 *Astrophys. J.* **134** 669–81
Sari R R and Merlini D 1976 *J. Stat. Phys.* **14** 91–100
Schwartz L 1965 *Méthodes Mathématiques pour les Sciences Physiques* (Paris: Hermann)
Wermer J 1974 *Potential Theory* (Berlin: Springer)
Wigner E P 1938 *Trans. Faraday Soc.* **34** 678