Contrib. Plasma Phys. **52**, No. 2, 153 – 156 (2012) / **DOI** 10.1002/ctpp.201100091

Physical Features of Binary Coulomb Crystals: Madelung Energy, Collective Modes and Phonon Heat Capacity

A. A. Kozhberov[*] and **D. A. Baiko**

Ioffe Physical-Technical Institute, Politekhnicheskaya 26, 194021 St. Petersburg, Russia
St. Petersburg State Polytechnical University, Politekhnicheskaya 29, 195251 St. Petersburg, Russia

Received 16 October 2011, revised 07 December 2011, accepted 05 January 2012
Published online 27 February 2012

Key words Coulomb crystal, binary mixture.

Electrostatic energy, collective modes, and thermodynamic functions of a Coulomb crystal with equal number of ions of two different types and uniform charge-compensating electron background are studied using harmonic lattice model. Simple cubic and hexagonal lattices with *two* different ions in the elementary cell (we denote these lattices sc2 and h2, respectively) are considered. The static sc2 lattice is more tightly bound than the h2 one at any charge ratio of the constituent ions. The phonon spectra depend on the ion charge and mass ratio. An analysis shows that these binary Coulomb crystals are stable, if the charge ratio is not too different from 1 (about 3.6 for sc2 and 1.3 for h2 lattices) regardless of the mass ratio. Heat capacity of the sc2 lattice is obtained by numerical integration over the first Brillouin zone as a function of temperature and charge and mass ratios. Well known classic and quantum asymptotes of the heat capacity are reproduced, and the dependence of the coefficient in the Debye T^3 law on charge and mass ratios is presented.

1 Introduction

The model of point charges (hereafter, ions) immersed into the uniform neutralizing background of opposite charge is in use in various branches of physics. At sufficiently low temperatures this system is known to crystallize with formation of a so-called Coulomb crystal. Typically, Coulomb crystals with only one ion type are considered. However, Coulomb crystal mixtures may be important for applications. In astrophysics, Coulomb crystal mixtures are expected to form in C/O cores of white dwarfs and in accreted envelopes of neutron stars. In this work we use harmonic lattice model to study main physical properties of binary Coulomb crystal mixtures composed of an equal number of ions with two different charges and masses. We consider simple cubic lattice with two different ions in the elementary cell (sc2). This lattice coincides with the body-centered cubic (bcc) lattice if all ions are the same. We also study phonon modes of the hexagonal lattice with two different ions in the elementary cell (h2). This lattice coincides with the hexagonal close-packed (hcp) lattice for identical ions.

2 Madelung energy

The position of an ion of type p (p-ion; for a binary mixture $p = 1$ or 2) in a crystal is given by its radius vector $\mathbf{r}_{lp} = \mathbf{X}_{lp} + \mathbf{u}_{lp}$, where $\mathbf{X}_{lp} = \mathbf{R}_l + \boldsymbol{\chi}_p$ is the equilibrium ion position in the crystal, and $\mathbf{u}_{lp}$ is the ion displacement. In this case, $\mathbf{R}_l$ is a lattice vector and $\boldsymbol{\chi}_p$ is the so-called basis vector of the p-ion, which determines equilibrium position of the ion in the lattice elementary cell.

The potential energy of the crystal is given by

$$U = \frac{1}{2}{\sum_{lpl'p'}}' Z_p Z_{p'} \Phi(\mathbf{r}_{lp} - \mathbf{r}_{l'p'}) - n_e \sum_{lp} Z_p \int \mathrm{d}\mathbf{r}\, \Phi(\mathbf{r}_{lp} - \mathbf{r}) + \frac{n_e^2}{2} \int\int \mathrm{d}\mathbf{r}\, \mathrm{d}\mathbf{r}'\, \Phi(\mathbf{r} - \mathbf{r}')\,, \quad (1)$$

[*] Corresponding author. E-mail: kozhberov@gmail.com

where $\Phi(\mathbf{r}) = e^2/r$, prime at the first sum means that terms with $l = l'$ and $p = p'$ are omitted, Z_p is the charge number of the p-ion, while n_e is the electron number density. For binary mixtures considered in this work $n_e = 0.5n(Z_1 + Z_2)$, where n is the number density of all ions.

If all ions are fixed at their equilibrium positions, $\mathbf{r}_{lp} = \mathbf{X}_{lp}$, Eq. (1) yields the Madelung energy U_0. We have derived rapidly converging expressions for calculating Madelung energy for arbitrary number of ions of different types in the lattice elementary cell. For binary mixtures in consideration

$$U_0 = N\frac{e^2}{a}\left[\frac{Z_1^2 + Z_2^2}{2^{4/3}}\zeta_1 + Z_1Z_2\left(\zeta_2 - \frac{\zeta_1}{2^{1/3}}\right)\right], \tag{2}$$

where N is the total number of all ions and $a = (4\pi n/3)^{-1/3}$ is the typical length scale. For the sc2 lattice, ζ_1 and ζ_2 are the Madelung constants of the simple cubic (sc) and bcc lattices, respectively. For the h2 lattice, ζ_1 and ζ_2 are the Madelung constants of the hexagonal and hcp lattices, respectively. It is clear that in the limits $Z_1 = Z_2$ and $Z_2 = 0$ we reproduce correctly the Madelung energy of respective single ion type crystals.

It is interesting to compare the Madelung energies of sc2 and h2 lattices with the same composition and matter density. The difference of the Madelung energies is $U_0^{\rm sc2} - U_0^{\rm h2} = Ne^2Z_1^2\Delta\zeta/a$, where $\Delta\zeta = 0.07978Z_2/Z_1 - 0.03993(1 + Z_2^2/Z_1^2)$. For any ratio Z_2/Z_1 the sc2 lattice Madelung energy is more negative than that of the h2 lattice. The minimum difference ($\Delta\zeta = -0.000091$) takes place at $Z_2/Z_1 = 0.99886 \approx 1$.

3 Dynamic matrix and collective modes

In the harmonic lattice model the potential energy Eq. (1) is expanded in powers of ion displacements. The second order term determines the dynamic matrix $D_{pp'}^{\alpha\beta}(\mathbf{k})$. This is a $3N_{\rm cell} \times 3N_{\rm cell}$ matrix, which depends on the wavevector $\mathbf{k}$ from the first Brillouin zone of the reciprocal lattice. In this case, $N_{\rm cell}$ is the number of ions in the lattice elementary cell and p and p' go from 1 to $N_{\rm cell}$ ($N_{\rm cell} = 2$ for sc2 and h2 lattices).

In a stable lattice the eigennumbers of the dynamic matrix at any $\mathbf{k}$ are positive and represent squared frequencies of the collective modes (lattice phonons) with the given wavevector. Using Ewald transformations (e.g., Ref. [1]), we have derived rapidly converging expressions for dynamic matrix elements for arbitrary number of ions of different types in the lattice elementary cell. Here we only present the result of the derivation:

$$D_{pp'}^{\alpha\beta}(\mathbf{k}) = \frac{Z_pZ_{p'}e^2}{\sqrt{M_pM_{p'}}}V_{pp'}^{\alpha\beta} + \frac{Z_pe^2}{M_p}W_p^{\alpha\beta}\delta_{pp'}, \tag{3}$$

where Greek indices denote Cartesian components, and

$$V_{pp'}^{\alpha\beta} = \frac{4\pi n}{N_{\rm cell}}\sum_m \frac{(G_m^\alpha - k^\alpha)(G_m^\beta - k^\beta)}{|\mathbf{G}_m - \mathbf{k}|^2}\exp\left[-\frac{|\mathbf{G}_m - \mathbf{k}|^2}{4A^2} + i(\mathbf{G}_m - \mathbf{k})(\boldsymbol{\chi}_p - \boldsymbol{\chi}_{p'})\right] - \frac{4A^3}{3\sqrt{\pi}}\delta^{\alpha\beta}\delta_{pp'}$$
$$- \sum_l (1 - \delta_{pp'}\delta_{\mathbf{R}_l 0})\left\{\left(\frac{3Y_l^\alpha Y_l^\beta}{Y_l^2} - \delta^{\alpha\beta}\right)\left[\frac{\mathrm{erfc}(AY_l)}{Y_l^3} + \frac{2A}{\sqrt{\pi}Y_l^2}e^{-A^2Y_l^2}\right] + \frac{4A^3}{\sqrt{\pi}}\frac{Y_l^\alpha Y_l^\beta}{Y_l^2}e^{-A^2Y_l^2}\right\}e^{i\mathbf{k}\mathbf{R}_l}, \tag{4}$$

$$W_p^{\alpha\beta} = -\frac{4\pi n}{N_{\rm cell}}\sum_{p''}Z_{p''}{\sum_m}'\frac{G_m^\alpha G_m^\beta}{G_m^2}\exp\left[-\frac{G_m^2}{4A^2} + i\mathbf{G}_m(\boldsymbol{\chi}_p - \boldsymbol{\chi}_{p''})\right] + \frac{4A^3}{3\sqrt{\pi}}Z_p\delta^{\alpha\beta}$$
$$+ \sum_{lp''} Z_{p''}(1 - \delta_{pp''}\delta_{\mathbf{R}_l 0})\left\{\left(\frac{3S_l^\alpha S_l^\beta}{S_l^2} - \delta^{\alpha\beta}\right)\left[\frac{\mathrm{erfc}(AS_l)}{S_l^3} + \frac{2A}{\sqrt{\pi}S_l^2}e^{-A^2S_l^2}\right] + \frac{4A^3}{\sqrt{\pi}}\frac{S_l^\alpha S_l^\beta}{S_l^2}e^{-A^2S_l^2}\right\}. \tag{5}$$

In this case, $\mathbf{Y}_l = \mathbf{R}_l + \boldsymbol{\chi}_p - \boldsymbol{\chi}_{p'}$, $\mathbf{S}_l = \mathbf{R}_l + \boldsymbol{\chi}_p - \boldsymbol{\chi}_{p''}$, and A is an arbitrary parameter chosen so that sums over direct and reciprocal lattice vectors, $\mathbf{R}_l$ and $\mathbf{G}_m$, converge equally rapidly (e.g., $A = 1/a$). It is understood that all lattice sums must be extended to infinity, whereas sums over p'' go over all ions in the elementary cell.

The sum of $3N_{\rm cell}$ squared eigenfrequencies at any $\mathbf{k}$ is equal to the trace of the dynamic matrix Eq. (3). The latter can be shown to be equal to $\omega_{\rm s}^2 N_{\rm cell} = 4\pi ne^2\sum_{pp'}Z_pZ_{p'}/(M_pN_{\rm cell})$. For our binary mixtures, $\omega_{\rm s}^2 = \pi ne^2(Z_1 + Z_2)(Z_1/M_1 + Z_2/M_2)$, and the sum of squared frequencies at any $\mathbf{k}$ is equal to $2\omega_{\rm s}^2$. For

identical ions ω_s becomes the regular plasma frequency $\omega_p = \sqrt{4\pi n Z^2 e^2/M}$ and the sum of squared frequencies is equal to $2\omega_p^2$. This is the case where we describe a bcc lattice as an sc2 lattice with 6 eigenfrequencies at every $\mathbf{k}$ (see below). If $Z_2 = 0$ the sum of all frequencies will be equal to $2\omega_s^2 = 4\pi(n/2)Z_1^2 e^2/M_1$. In this limit we get an sc lattice with ion number density of $n/2$ and three frequencies at every $\mathbf{k}$ (the other three frequencies tend to zero in this limit).

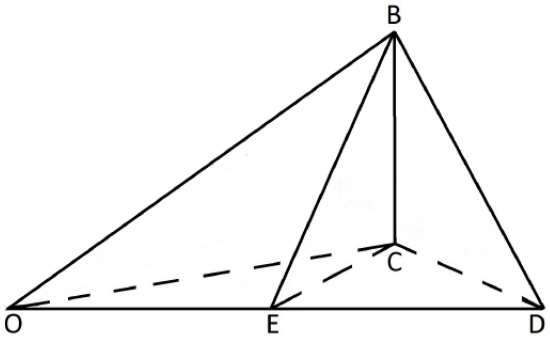

Fig. 1 The primitive subzone of the first Brillouin zone of the bcc lattice (OBCD) and of the sc2 lattice (OBCE).

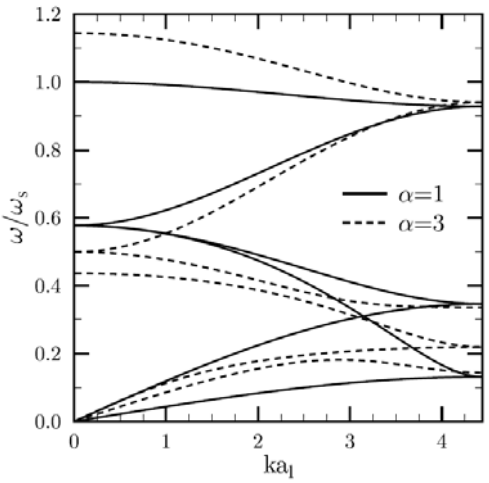

Fig. 2 Dispersion curves of the sc2 lattice along OC (Fig.1) for two values of α.

The primitive subzones OBCE and OBCD of the Brillouin zones of sc2 and bcc lattices, respectively, are shown in Fig. 1. In this case, O is the origin ($\mathbf{k} = 0$ point). If a_l is the sc lattice constant (so that $na_l^3 = 2$) then $\mathbf{k}a_l = (\pi, 0, 0)$ for point E, $\mathbf{k}a_l = (2\pi, 0, 0)$ for point D, $\mathbf{k}a_l = (\pi, \pi, 0)$ for point C, and $\mathbf{k}a_l = (\pi, \pi, \pi)$ for point B. The spectrum of the binary mixture depends on two parameters $\alpha = Z_2/Z_1$ and $\beta = M_2/M_1$. In Fig. 2 we show dispersion curves of the sc2 lattice with $\beta = 1$ and two values of $\alpha = 1$ and 3. These curves are drawn as functions of ka_l in the direction OC of Fig. 1. At $\alpha = 1$ we have bcc lattice of identical ions. Hence, three solid curves (the upper one and the two, which have $\omega = 0$ at $k = 0$) coincide with dispersion curves of the bcc lattice along OC. Three other modes of the sc2 lattice can be obtained from the bcc lattice modes if the domain of variation of k is reflected with respect to the plane BCE, which is the boundary of the sc2 lattice Brillouin zone. As a result of this reflection, OC becomes DC and, in particular, the origin is mapped onto the point D. This point is the vertex of the Brillouin zone of the bcc lattice, where the frequencies of all three modes of the bcc lattice coincide. This explains the merger of the three modes of the sc2 lattice at $ka_l = 0$ (Fig. 2).

As α exceeds 1, the mode crossing seen in Fig. 2 turns into avoided crossings. With further growth of α the sc2 lattice modes deviate from those of the bcc lattice more strongly. There is a critical value of the charge ratio $\alpha_{\rm crit}$, at which the minimum squared frequency at some finite $\mathbf{k}$ crosses zero and is negative at higher α. Our numerical experiments show that at point C it happens at the lowest α. This situation is illustrated in Fig. 3. We plot the minimum frequency at point C as a function of α for several values of β. All curves drop to zero at the same $\alpha_{\rm crit} \approx 3.6$ (irrespective of ion masses). At higher α the frequency of at least one mode is imaginary and the lattice is unstable. Similar stability analysis was performed for the h2 lattice. It becomes unstable at much lower $\alpha_{\rm crit} \approx 1.3$.

4 Phonon thermodynamics

Once the phonon spectrum is known, thermodynamic functions of the crystal can be calculated. For instance, specific heat is given by (e.g., Ref. [2])

$$C = \sum_{\mathbf{k}\nu} \frac{\hbar^2 \omega_{\mathbf{k}\nu}^2}{4T^2 \sinh^2(\hbar\omega_{\mathbf{k}\nu}/2T)}\,, \tag{6}$$

where T is the temperature and $\omega_{\mathbf{k}\nu}$ is the frequency of the phonon mode with wavevector $\mathbf{k}$ and polarization index ν. Summation over ν runs from 1 to 6, while summation over $\mathbf{k}$ implies integration over the first Brillouin zone. The methods of such integration have been developed elsewhere (Ref. [3], see also [4]).

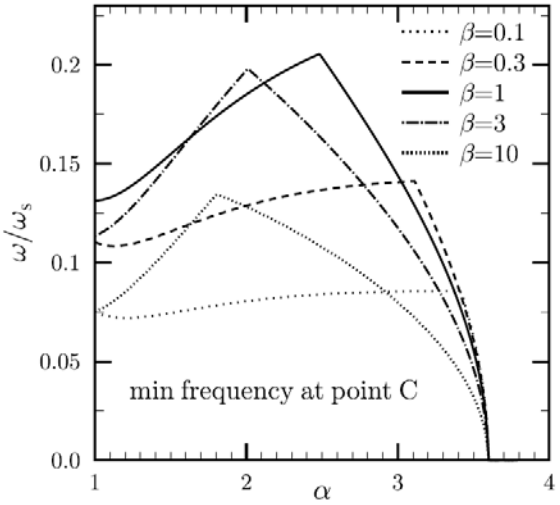

Fig. 3 Minimum frequency of the sc2 lattice at point C (Fig.1) as a function of α for several values of β.

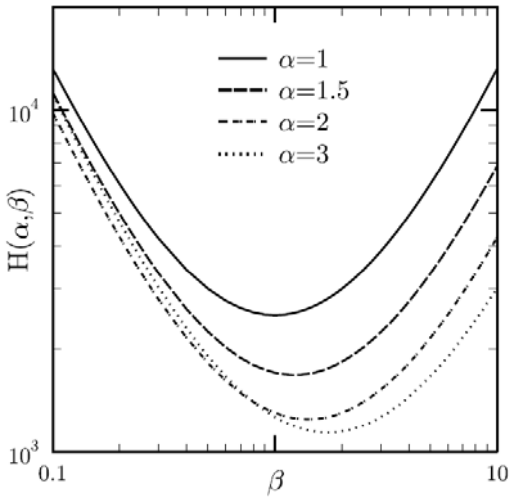

Fig. 4 The coefficient of the Debye T^3 dependence of the heat capacity vs. β for several values of α (sc2 lattice).

It is well known that at high temperatures, $T \gtrsim T_\mathrm{s} \equiv \hbar\omega_\mathrm{s}$, $C \approx 3N$. At low temperatures Debye T^3 law must take place $C/N = H(\alpha,\beta)(T/T_\mathrm{s})^3$. These asymptotic behaviors are observed at all considered α and β. The dependence of H on β for several values of α for the sc2 lattice is shown in Fig. 4. The value of $H \approx 2512$ at $\alpha = \beta = 1$ reproduces calculations of heat capacity for bcc crystal of identical ions [4]. The growth of $H(\alpha,\beta)$ at large and small β is explained by the fact that $H/T_\mathrm{s}^3 \propto v^{-3}$, where v is an average phase velocity of acoustic phonons, which are responsible for the T^3 dependence of the specific heat ($v \propto \sqrt{1/M_\mathrm{max}}$), while $T_\mathrm{s} \propto \sqrt{1/M_\mathrm{min}}$ (at $\alpha \sim 1$). Accordingly, H grows as $\beta^{3/2}$ at $\beta \gg 1$ and as $\beta^{-3/2}$ at $\beta \ll 1$.

5 Conclusion

We have studied electrostatic energy, phonon modes and heat capacity of a Coulomb crystal mixture composed of equal number of ions of two different types with uniform neutralizing electron background. It is shown that static sc2 lattice is more tightly bound than h2 lattice for any charge ratio of constituent ions. Rapidly convergent expression for the dynamic matrix of an arbitrary Coulomb crystal mixture is obtained. Phonon modes of the sc2 and h2 lattices are analyzed and it is shown that these lattices become unstable at the charge ratio of about 3.6 for sc2 and 1.3 for h2, regardless of the mass ratio of constituent ions. Finally, heat capacity of the sc2 lattice is calculated by numerical integration and the coefficient of its quantum T^3 asymptote is presented as a function of ion charge and mass ratios.

Acknowledgements The authors are deeply grateful to D.G. Yakovlev, who suggested the topic of this research, and to G. Kalman, H.E. DeWitt, and A.I. Chugunov for enlightening discussions. The work was supported by Rosnauka (grant NSh 3769.2010.2). DAB is also grateful to the Ministry of Education and Science of Russian Federation (contract No. 11.G34.31.0001), and to the RFBR (grant 11-02-00253-a).

References

[1] M. Born, K. Huang, Dynamical Theory of Crystal Lattices. Izdatelstvo inostrannoi literatury, Moscow 1954.
[2] L.D. Landau, E.M. Lifshitz, Statistical Physics. Part I. Pergamon Press, Oxford 1980.
[3] R.C. Albers, J.E. Gubernatis, Los Alamos Scientific Laboratory Report No. LA-8674-MS 1981.
[4] D.A. Baiko, A.Y. Potekhin, D.G. Yakovlev, Phys. Rev. E **64**, 057402 (2001).

