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Thermodynamic functions of harmonic Coulomb crystals

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Phonon frequency moments and thermodynamic functions (electrostatic and vibrational parts of the free energy, internal energy, and heat capacity) are calculated for bcc and fcc Coulomb crystals in the harmonic approximation with a fractional accuracy $\lesssim 10^{-5}$. Temperature dependence of thermodynamic functions is fitted by analytical formulas with an accuracy of a few parts in 10^5. The static-lattice (Madelung) part of the free energy is calculated with an accuracy of $\sim 10^{-12}$. The Madelung constant and frequency moments of hcp crystals are also computed.

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I. INTRODUCTION

Coulomb crystals, introduced into theory by Wigner [1], were studied by many authors. A thorough discussion was given, e.g., in Refs. [2,3]. The Ewald technique [4,5] was used to calculate shear constants [6] and dispersion relations [7] of such crystals. Thermodynamics in the harmonic-lattice approximation was analyzed, e.g., in Refs. [3,8,9]. Anharmonic corrections were discussed in Refs. [10–12]. Chabrier *et al.* [13] suggested an approximate analytical model of the harmonic Coulomb crystal, which is widely used in astrophysics (e.g., Refs. [9,14,15]). However, precise numerical calculations of the thermodynamic functions, valid at any temperature T, have not been published.

Here we report highly accurate calculations of phonon spectra and frequency moments of body-centered-cubic (bcc), face-centered-cubic (fcc), and hexagonal-close-packed (hcp) one-component Coulomb lattices in the harmonic approximation. We also present accurate calculations of thermodynamic functions for bcc and fcc lattices at any values of the quantum parameter $\theta = T_p/T$, where $T_p = \hbar\omega_p/k_B$ is the ion plasma temperature and $\omega_p = \sqrt{4\pi n_i Z^2 e^2/M}$ is the ion plasma frequency (n_i, M, and Ze being the ion number density, mass, and charge, respectively). The numerical results are given in the easy-to-use form of tables and fitting formulas.

II. PHONON SPECTRUM AND ELECTROSTATIC ENERGY

Consider a crystal of identical ions immersed in the uniform compensating background. The basic definitions are as follows (see, e.g., Ref. [5]). Let us take an arbitrary ion as the origin of a Cartesian reference, frame and specify the lattice basis $\mathbf{l}_1, \mathbf{l}_2, \mathbf{l}_3$ generating direct lattice vectors $\mathbf{l}(n_1, n_2, n_3) = n_1\mathbf{l}_1 + n_2\mathbf{l}_2 + n_3\mathbf{l}_3$, where n_1, n_2, and n_3 are arbitrary integers. The vectors $\mathbf{g}(n_1, n_2, n_3) = n_1\mathbf{g}_1 + n_2\mathbf{g}_2 + n_3\mathbf{g}_3$, where $\mathbf{g}_i \cdot \mathbf{l}_j = 2\pi\delta_{ij}$, form the reciprocal lattice. Also consider the primitive cell, the parallelepiped $\{\nu_1\mathbf{l}_1 + \nu_2\mathbf{l}_2 + \nu_3\mathbf{l}_3\}$, with $0 \leqslant \nu_1, \nu_2, \nu_3 < 1$. Let N_{cell} be the number of ions in the primitive cell enumerated with an index k. The choice of the vectors $\mathbf{l}_i$ is not unique, and one can describe a given lattice using different N_{cell}. We will adopt the standard convention and choose the primitive cell with the lowest N_{cell}. The bcc and fcc lattices are simple (the lowest $N_{\text{cell}} = 1$), whereas for the hcp lattice one has the lowest $N_{\text{cell}} = 2$.

Along with the primitive cell one usually considers the Wigner-Seitz (WS) cell, which is a polyhedron with faces crossing the lattice vectors at their midpoints at the right angle. The volume of the WS cell is equal to that of the primitive cell, N_{cell}/n_i. A convenient measure of interparticle spacing is the ion-sphere radius $a = (3/4\pi n_i)^{1/3}$. The WS cell of the reciprocal lattice is the first Brillouin zone (BZ); its volume is equal to $V_{BZ} = (2\pi)^3 n_i$.

The frequencies ω_s and polarization vectors $\mathbf{e}_s$ of lattice vibrations ($s = 1, \ldots, 3N_{\text{cell}}$ enumerates vibration modes) at any point $\mathbf{q}$ of the BZ are determined by (e.g., Ref. [5])

$$\frac{\omega^2}{\omega_p^2} e_s^{\alpha k} - \sum_{k'\beta} \mathcal{D}_{\alpha\beta}(k,k',\mathbf{q}) e_s^{\beta k'} = 0, \tag{1}$$

where the summation is over three Cartesian coordinates (Greek indices) and over the ions in the primitive cell (k');

$$\mathcal{D}_{\alpha\beta}(k,k',\mathbf{q}) = \frac{1}{3}\delta_{\alpha\beta}\delta_{kk'} - \frac{a^3}{3}\left(\frac{\partial^2}{\partial u_\alpha \partial u_\beta} {\sum_{\mathbf{l}}}' \frac{\mathrm{e}^{-i\mathbf{q}\cdot\mathbf{l}}}{|\mathbf{r}-\mathbf{u}|} \right)_{\mathbf{u}\to 0} \tag{2}$$

is the dynamical matrix, $\mathbf{r} = \mathbf{l} + \mathbf{x}(k) - \mathbf{x}(k')$, and $\mathbf{x}(k)$ specifies the ion position within the primitive cell. The primed sum means that the term $\mathbf{l} = 0$ is excluded if $k = k'$.

The elements of the dynamical matrix can be calculated using the Ewald technique of θ-function transformations (e.g., Ref. [5]), which yields

$$\begin{aligned}\mathcal{D}_{\alpha\beta}(k,k',\mathbf{q}) = {} & \frac{1}{3}\,\delta_{\alpha\beta}\delta_{kk'} - \frac{4\rho^3 a^3}{9\sqrt{\pi}}\,\delta_{\alpha\beta}\delta_{kk'} \\ & - {\sum_{\mathbf{l}}}' \left[\rho^3 a^3 \frac{4}{3\sqrt{\pi}} \frac{r_\alpha r_\beta}{r^2} e^{-\rho^2 r^2} \right. \\ & + \frac{\rho a^3\,(3 r_\alpha r_\beta - \delta_{\alpha\beta} r^2)}{3 r^4} \\ & \left. \times \left(\frac{\operatorname{erfc}(\rho r)}{\rho r} + \frac{2}{\sqrt{\pi}} e^{-\rho^2 r^2} \right) \right] e^{-i\mathbf{q}\cdot\mathbf{l}}\end{aligned}$$

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TABLE I. Parameters of Coulomb crystals.

Lattice type	K_M	$\langle(\omega/\omega_p)^{-2}\rangle$	$\langle(\omega/\omega_p)^{-1}\rangle$	$\langle(\omega/\omega_p)\rangle$	$\langle(\omega/\omega_p)^{3}\rangle$	$\langle\ln(\omega/\omega_p)\rangle$
bcc	−0.895 929 255 682	12.972	2.798 55	0.511 3875	0.250 31	−0.831 298
fcc	−0.895 873 615 195	12.143	2.719 82	0.513 1940	0.249 84	−0.817 908
hcp	−0.895 838 120 459	12.015	2.7026	0.513 33	0.249 84	−0.815 97

$$+\frac{1}{N_{\rm cell}}\sum_{\mathbf{g}}\frac{(g_\alpha-q_\alpha)(g_\beta-q_\beta)}{|\mathbf{g}-\mathbf{q}|^2}\times\exp\left(-\frac{|\mathbf{g}-\mathbf{q}|^2}{4\rho^2}-i(\mathbf{g}-\mathbf{q})\cdot[\mathbf{x}(k)-\mathbf{x}(k')]\right). \tag{3}$$

The last sum is over all reciprocal lattice vectors, and ρ is a free parameter adjusted to yield equally rapid convergences of direct and reciprocal sums; a suitable choice is $\rho a\approx 2$. Numerical calculations according to Eq. (3) become unstable at $qa\ll 1$ (near the BZ center). In this region we replace $D_{\alpha\beta}$ by an appropriate asymptote [16], whose coefficients have been recalculated with an accuracy $\sim 10^{-8}$ using the Ewald technique.

The static-lattice binding energy of a Coulomb lattice is

$$E_0=K_M Z^2 e^2/a, \tag{4}$$

where the Madelung constant K_M can be written as

$$K_M=\frac{a}{2N_{\rm cell}}\sum_{k',k}\sum_{\mathbf{l}}{}'\frac{\mathrm{erfc}(\rho r)}{r}-\frac{3}{8\rho^2a^2}-\frac{\rho a}{\sqrt{\pi}}+\frac{3}{2N_{\rm cell}^2}\sum_{k',k}\sum_{\mathbf{g}}{}'\frac{1}{g^2a^2}\times\exp\left(-\frac{\mathbf{g}^2}{4\rho^2}+i\mathbf{g}\cdot[\mathbf{x}(k)-\mathbf{x}(k')]\right). \tag{5}$$

Previously K_M was calculated, e.g., in Refs. [17,18]. Our calculated values of K_M for bcc, fcc, and hcp crystals are given in Table I.

III. BZ INTEGRATION AND FREQUENCY MOMENTS

In many physical problems, one needs to average functions $f(\omega)$ over phonon branches and wave vectors:

$$\langle f\rangle=\frac{1}{3N_{\rm cell}}\sum_s\bar{f},\quad \bar{f}=\frac{1}{V_{BZ}}\int_{\rm BZ}f(\mathbf{q})\,\mathrm{d}\mathbf{q}, \tag{6}$$

where $f(\mathbf{q})\equiv f(\omega_s(\mathbf{q}))$. In Eq. (6) we will use the Holas integration method considered in Ref. [19] for the bcc lattice:

$$\bar{f}=\int_0^1 d\xi\int_0^1 d\eta\int_0^1 d\zeta\,\eta\xi^2\mathcal{F}\{f\}, \tag{7}$$

where ξ, η, and ζ are appropriate BZ coordinates. For the bcc crystal, $\mathcal{F}\{f\}=6f(\mathbf{q})$, with $\mathbf{q}\equiv(q_x,q_y,q_z)=(2-\eta,\eta,\eta\zeta)\pi\xi/a_l$, and the lattice constant a_l is given by $n_i a_l^3=2$. We calculate the integrals in Eq. (7) by the Gauss method involving the nodes of the Jacobi polynomials $P_n^{(0,0)}$. The integral over η is alternatively treated by the generalized Gauss scheme with weight function η, which involves the nodes of $P_n^{(1,0)}$.

This approach can also be developed for fcc and hcp lattices. In both cases we again come to Eq. (7), but with different $\mathcal{F}\{f\}$. For the fcc lattice, we have $\mathcal{F}\{f\}=\frac{3}{2}[\frac{3}{2}f(\mathbf{q}_1)+\frac{3}{2}f(\mathbf{q}_2)+f(\mathbf{q}_3)]$, where $\mathbf{q}_i=\mathbf{Q}_i\pi\xi/(2a_l)$, $\mathbf{Q}_1=(2+\eta+\eta\zeta,2+\eta-\eta\zeta,2-2\eta)$, $\mathbf{Q}_2=(2+2\eta,2-\eta+\eta\zeta,2-\eta-\eta\zeta)$, $\mathbf{Q}_3=(4,\eta+\eta\zeta,\eta-\eta\zeta)$, and $n_i a_l^3=4$.

For the hcp lattice, $\mathcal{F}\{f\}=2f(\mathbf{q}_1)/\eta+2f(\mathbf{q}_2)$, where $\mathbf{q}_i=\mathbf{Q}_i 2\pi\xi/(3a_l)$, $\mathbf{Q}_1=(\sqrt{3},\zeta,\frac{3}{2}\eta/\sigma)$, $\mathbf{Q}_2=(\eta\sqrt{3},\eta\zeta,\frac{3}{2}/\sigma)$, and $n_i a_l^3=\sqrt{2}$. Here $\sigma=\sqrt{8/3}$ is twice the ratio of the distance between the hcp lattice planes to the distance between neighbors within one plane.

Phonon frequency moments $\langle(\omega/\omega_p)^n\rangle$, and the average $\langle\ln(\omega/\omega_p)\rangle$, obtained by this method, are given in Table I. We remind the reader that $\langle(\omega/\omega_p)^2\rangle=\frac{1}{3}$, according to the Kohn rule (e.g., Ref. [17]). The accuracy of the data in Table I corresponds to the number of digits shown; it is the same or higher than the accuracy of the previous results (e.g., Refs. [11,17,19,20]), except only the value of $\langle\omega/\omega_p\rangle$ for the hcp lattice, calculated more accurately in Ref. [20] ($\langle\omega/\omega_p\rangle_{\rm hcp}=0.5133368$).

IV. THERMODYNAMIC FUNCTIONS

The free energy F of a harmonic Coulomb crystal consists of the static-lattice contribution E_0; the contribution from zero-point ion vibrations, $\frac{3}{2}N\hbar\langle\omega\rangle$; and thermal free energy in the harmonic lattice approximation, $F_{\rm th}$. Accordingly, the reduced free energy $f\equiv F/(Nk_BT)$ is

$$f=K_M\Gamma+1.5\langle w\rangle+f_{\rm th}, \tag{8}$$

where $f_{\rm th}(\theta)=3\langle\ln(1-e^{-w})\rangle$, and

$$\Gamma=\frac{(Ze)^2}{ak_BT},\quad w=\frac{\hbar\omega}{k_BT}=\theta\frac{\omega}{\omega_p}.$$

Thus the reduced internal energy $u\equiv U/(Nk_BT)=-\partial f/\partial\ln T$ is

$$u=K_M\,\Gamma+1.5\langle w\rangle+u_{\rm th}, \tag{9}$$

where

TABLE II. Parameters of the analytical approximation [Eq. (13)] of the thermal free energies of bcc and fcc Coulomb lattices. Powers of 10 are given in square brackets.

	bcc lattice			fcc lattice		
n	α_n	a_n	b_n	α_n	a_n	b_n
0		1	261.66		1	303.20
1	0.932446	0.1839	0	0.916707	0	0
2	0.334547	0.593586	7.07997	0.365284	0.532535	7.7255
3	0.265764	5.4814[−3]	0	0.257591	0	0
4		5.01813[−4]	0.0409484		3.76545[−4]	0.0439597
5		0	3.97355[−4]		0	1.14295[−4]
6	4.757014[−3]	3.9247[−7]	5.11148[−5]	4.92387[−3]	2.63013[−7]	5.63434[−5]
7		0	2.19749[−6]		0	1.36488[−6]
8	4.7770935[−3]	5.8356[−11]		4.37506[−3]	6.6318[−11]	

$$u_{\mathrm{th}}(\theta)=\frac{d f_{\mathrm{th}}}{d \ln \theta}=3\left\langle \frac{w}{e^{w}-1}\right\rangle . \qquad (10)$$

The harmonic constituent of the reduced heat capacity, $c_V=(Nk_B)^{-1}\partial U/\partial T=u+\partial u/\partial \ln T$, is

$$c_V(\theta)=u_{\mathrm{th}}-\frac{d u_{\mathrm{th}}}{d \ln \theta}=3\left\langle \frac{w^2 e^{-w}}{(1-e^{-w})^2}\right\rangle . \qquad (11)$$

Using the results of Secs. II and III, we have calculated $f_{\mathrm{th}}(\theta)$, $u_{\mathrm{th}}(\theta)$, and $c_V(\theta)$ for bcc and fcc crystals as corresponding BZ averages. The mean numerical error is estimated as $\sim 10^{-6}$, and it is a few times larger at $\theta \gg 1$. Let us discuss possible analytical approximations. The model of Chabrier *et al.* [13] assumed a linear dispersion law for two acoustic (Debye-type) modes, $\omega_\perp=\alpha\omega_p q/q_B$, and an optical (Einstein-type) mode, $\omega_\parallel=\gamma\omega_p$. The known phonon spectrum moments of a Coulomb crystal are approximately reproduced with the choice $\alpha\approx 0.4$, $\gamma\approx 0.9$. In this model,

$$f_{\mathrm{th}}=2\ln(1-e^{-\alpha\theta})+\ln(1-e^{-\gamma\theta})-\frac{2}{3}D_3(\alpha\theta), \qquad (12)$$

where $D_3(z)\equiv(3/z^3)\int_0^z t^3/(e^t-1)\,dt$ is the Debye function. This model reproduces numerical values of f_{th}, u_{th}, and c_V with an accuracy of $\sim 10\%$.

A heuristic generalization of Eq. (12) provides a convenient fitting formula to f_{th}. Introducing three logarithmic terms (according to three phonon modes) and replacing D_3 by an arbitrary rational-polynomial function possessing the correct asymptote $\propto \theta^{-3}$ at large θ, we obtain

$$f_{\mathrm{th}}=\sum_{n=1}^{3}\ln(1-e^{-\alpha_n\theta})-\frac{A(\theta)}{B(\theta)}, \qquad (13)$$

where

$$A(\theta)=\sum_{n=0}^{8} a_n\theta^n,$$

$$B(\theta)=\sum_{n=0}^{7} b_n\theta^n+\alpha_6\, a_6\,\theta^9+\alpha_8\, a_8\,\theta^{11}; \qquad (14)$$

the parameters α_n, a_n, and b_n are given in Table II.

Calculation of the harmonic thermal energy and heat capacity from Eq. (13) using Eqs. (10) and (11), yields

$$u_{\mathrm{th}}=\sum_{n=1}^{3}\frac{\alpha_n\theta}{e^{\alpha_n\theta}-1}-\theta\frac{A'(\theta)B(\theta)-A(\theta)B'(\theta)}{B^2(\theta)}, \qquad (15)$$

$$c_V=\sum_{n=1}^{3}\frac{\alpha_n^2\theta^2}{(e^{\alpha_n\theta/2}-e^{-\alpha_n\theta/2})^2} +\theta^2\frac{A''B^2-2A'B'B+2A(B')^2-ABB''}{B^3}, \qquad (16)$$

where the first and second derivatives A', A'', B', and B'' are readily obtained from Eq. (14). Approximations (13), (15), and (16) have a fractional accuracy within 5×10^{-6}, 2×10^{-5}, and 5×10^{-5}, respectively.

In the classical limit $\theta\to 0$, the exact expansion of f_{th} is

$$f_{\mathrm{th}}=3\ln\theta+3\left\langle \ln\left(\frac{\omega}{\omega_p}\right)\right\rangle-\frac{3}{2}\left\langle\frac{\omega}{\omega_p}\right\rangle\theta+\frac{1}{24}\theta^2+\cdots. \qquad (17)$$

Note that the term $-\frac{3}{2}\langle\omega/\omega_p\rangle\theta$ cancels the zero-point energy in Eq. (8). Our fit [Eq. (13)] reproduces the logarithmic, constant, and linear terms of Eq. (17) exactly (by construction), whereas the last (quadratic) term is reproduced with the relative accuracy of 5×10^{-5} and 10^{-6} for bcc and fcc lattices, respectively. Although we do not present calculations of the thermal thermodynamic functions for hcp crystals, our analysis reveals that they do not deviate from the functions for fcc crystals by more than a few parts in 10^3. Our results can be used in any applications which require a fast and accurate evaluation of the thermodynamic functions of the Coulomb crystals.

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