Thermodynamic properties of Coulomb crystals with isotopic impurities

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Abstract. This work is devoted to a description of Coulomb crystals with isotopic impurities which are expected to be formed in degenerate stars interiors. We consider the case when the mass of impurities $M'$ is slightly different from the mass of 'basic' ions $M$ while fraction of impurities can be arbitrary. It is shown that the heat capacity perturbation theory of disordered crystals is in a good agreement with the linear mixing theory and with the exact calculations for binary crystals.

1. Introduction
It is generally accepted that matter in white dwarf cores and neutron star crusts consists of fully ionized atomic nuclei and uniform charge-neutralizing background of degenerate electrons. As a star cools, ions are expected to crystallize into a body-centered cubic (bcc) lattice. The resulting state of matter could be described by the Coulomb crystal model (e.g., [1]).

Usually, dense plasmas in astrophysical settings contain several different species of ions, either as principal constituents or as impurities. The interior of white dwarfs is thought to be composed of a carbon and oxygen crystal mixture with traces of other elements such as neon and iron. In the inner crust of neutron stars nuclei are neutron-rich and at a given density several neutron-rich isotopes of a single nuclei may be present.

In this paper we continue our study of thermodynamic properties of Coulomb crystals with isotopic impurities started in [2]. The case when the mass of impurities is not much different from the mass of 'basic' ions is considered (their number density can be arbitrary). The obtained results for the heat capacity are compared with the results given by the linear mixing theory [3] and with the exact calculations for the perfectly ordered binary Coulomb crystals [4].

2. Phonon density of states of the Coulomb bcc lattice
Phonon spectrum $\omega_i(k)$ of a bcc Coulomb crystal lattice at any wavevector $k$ can be found by solving the dispersion equation,

$$\det\{D^{\alpha\beta}(k) - \omega_i^2(k)\delta^{\alpha\beta}\} = 0,$$

where $D^{\alpha\beta}(k)$ is the dynamic matrix (e.g., [5]), $\alpha$ and $\beta$ are Cartesian coordinates. Index $i$ enumerates oscillation modes at given $k$. The bcc lattice has one ion in the elementary cell so $i = 1, 2, 3$. It is useful to measure the phonon frequencies in terms of plasma frequency:
\[ \omega_0^2 = 4\pi NZ^2e^2/(VM), \]

where \( N \) is the total number of ions, \( V \) is the volume, while \( Z \) and \( M \) are the charge number and mass of ions, respectively.

One of the important characteristic of the phonon spectrum is the phonon density of states

\[ \nu(\omega/\omega_p) = \int \frac{\omega_p}{3N} \sum_{k_i} \delta(\omega - \omega_i(k)), \]

where sum comes over all oscillation modes and wavevectors in the first Brillouin zone. The density of states is usually normalized as \( \int_0^\infty dx \nu(x) = 1 \). Since the maximum phonon frequency of the bcc lattice is \( \omega_p \), the integration upper limit is taken to be equal to 1. The phonon density of states of this lattice is shown in Fig. 1.

![Phonon density of states](image)

**Figure 1.** Phonon density of states of the Coulomb bcc lattice.

Any phonon thermodynamic function can be calculated using \( \nu(x) \). For instance, the phonon heat capacity is given by

\[ C = 3N \int_0^1 dx \nu(x) \varphi(x, t), \quad \varphi(x, t) = \frac{x^2 \exp(x/t)}{t^2[\exp(x/t) - 1]^2}, \]

where \( t \equiv T/T_p, T_p \equiv \hbar \omega_p/k_B \) is the ion plasma temperature, \( k_B \) is the Boltzmann constant.

3. Impurity contribution to crystal thermodynamics

Modification of the thermodynamics properties due to the presence of an isotopic impurity has been described in a number of works on solid-state physics [6, 7, 8, 9]. Here, we apply to the Coulomb crystals the perturbation theory of disordered crystal spectra developed by Lifshitz in [6, 7].

Generally mass of the isotopic impurities \( M' \) is not much different from the mass of other ions in a crystal \( M \). Hence we can write an expansion of any thermodynamic quantity in powers of \( \varepsilon \equiv (M' - M)/M \) [7]. For the heat capacity the first two terms of this expansion could be
written as

\[
\frac{C_{\text{eps}}}{N} = \frac{C}{N} + \frac{\Delta C_{\text{eps}}}{N} = \frac{C}{N} - \frac{\varepsilon n}{2} \int_0^1 dx x \varphi'(x,t) \nu(x) \\
+ \frac{\varepsilon^2}{2} \left[ n^2 \int_0^1 dx x \left\{ \varphi'(x,t) + \frac{\varphi''(x,t)x}{4} \right\} \nu(x) \\
+ n (1 - n) \int_0^1 dx x^3 \varphi'(x,t) \nu(x) \int_0^1 \frac{\nu(x')}{x^2 - x'^2} dx' \right], \tag{4}
\]

where \( n = N_{\text{imp}}/N \), and \( N_{\text{imp}} \) is the number of impurities (0 ≤ n ≤ 0.5). \( C \) is the heat capacity of a perfect crystal of ions with mass \( M \). The integration in the last term is understood in the sense of the principal value.

The temperature dependence of \( \Delta C_{\text{eps}}/C \) has two asymptotes. At high temperatures \( \Delta C_{\text{eps}}/C \propto T^{-2} \) because \( \varphi(x,t) \approx 1 - x^2/(12t^2) \) at \( t \gg 1 \), while \( C \approx 3N \). At low temperatures \( C \propto T^3 \) and \( \Delta C_{\text{eps}}/C \approx 1.5n\varepsilon + 0.375n^2\varepsilon^2 \) [8]. Both asymptotes are reproduced in our calculations and can be observed in Fig. 2, where ratios \( \Delta C_{\text{eps}}/C \) are plotted for several values of \( n \) at \( \varepsilon = 0.1 \).

One can apply Eq. (4) to a Coulomb crystal with \( N_{\text{imp}} = N/2 \). At \( |\varepsilon| \ll 1 \) the received result can be compared with the exact calculations for the heat capacity of the perfectly ordered binary Coulomb crystal [4]. In [4] the heat capacity of a binary Coulomb crystal with the one-to-one ratio of ions with different masses is considered as a function of \( T/T_s \) and \( M'/M \), where

\[
T_s = T_p \sqrt{\varepsilon + 2}/(2\varepsilon + 2)
\]

is the effective ion plasma temperature of the mixture. For the binary crystal heat capacity can be written as

\[
C_{\text{bin}} = C + \Delta C_{\text{bin}}. \tag{5}
\]

At \( \varepsilon = 0.1 \) the ratio \( \Delta C_{\text{bin}}/C \) is shown by circles in Fig. 2. It is clear to see that the perturbation theory proposed by Lifshitz gives results which are in a very good agreement with the exact calculations. At \( \varepsilon = 0.1 \) maximum of ratio \( (\Delta C_{\text{bin}} - \Delta C_{\text{eps}})/\Delta C_{\text{eps}} \) is less than 0.01. Also we can conclude that the difference between heat capacity of ordered and disordered Coulomb crystals is small and could be neglected during simulations of degenerate stars.

**Figure 2.** Ratio of \( \Delta C_{\text{eps}} \) to \( C \) for several values of \( n \) at \( \varepsilon = 0.1 \).

**Figure 3.** Ratio of \( \Delta C_{\text{eps}} \) to \( \Delta C_{\text{bin}} \) for several values of \( n \) and \( \varepsilon \).
4. Comparison with linear mixing theory

Typically, the thermodynamic properties of classical Coulomb mixtures are calculated using the linear mixing theory [3]. In this approach, the phonon heat capacity of a binary mixture is equal to

\[ C_{lm} = (1 - n)C + nC' = C + \Delta C_{lm}, \]  

where \( C' \) is the specific heat of a crystal composed of ions with mass \( M' \) at the same temperature as ‘basic’ crystal. Previously the linear mixing theory was verified in [4] for the binary bcc lattice, so only for the crystal with \( n = 0 \).

Here we can compare \( \Delta C_{lm} \) and \( \Delta C_{eps} \) for \( j \ll 1 \) and for any \( n \). At high temperatures \( \Delta C_{lm} \approx n \varepsilon/(1 + \varepsilon)/(12t^2) \) while \( \Delta C_{eps} \approx n[\varepsilon - \varepsilon^2]/(12t^2) \). Hence at \( T \gg T_p \) ratio \( \Delta C_{eps}/\Delta C_{lm} \approx 1 - \varepsilon^2 \) and does not depend on \( n \). It could be seen in Fig. 3, where this ratio is plotted at high and medium temperatures. For \( n \) and \( \varepsilon \) in consideration \( |\Delta C_{eps}/\Delta C_{lm} - 1| \) is always less than 0.03.

The low temperature limit is not plotted in Fig. 3 because it is not achieved at \( T = 10^{-2}T_p \). At \( T \ll T_p \) \( \Delta C_{lm} \approx nC[(\varepsilon + 1)^{3/2} - 1] \) while \( \Delta C_{eps} \approx nC[1.5\varepsilon + 0.375n\varepsilon^2] \). So at low temperatures and \( |\varepsilon| \ll 1 \) \( \Delta C_{eps}/\Delta C_{lm} \rightarrow 1 + \varepsilon(n-1)/4 \) and the difference between \( \Delta C_{eps} \) and \( \Delta C_{lm} \) increases with \( n \) decreases. This behaviour could be traced in Fig. 3 at even \( T \sim 10^{-2}T_p \).

5. Conclusions

We have used the Lifshitz perturbation theory to calculate changes of the Coulomb crystal heat capacity due to the isotopic impurities \( \Delta C_{eps} \) when the difference between masses of ‘basic’ ions and impurities is small. At high temperatures these changes \( \Delta C_{eps} \) decay as \( T^{-2} \), while \( \Delta C_{eps}/C \approx 1.5n\varepsilon + 0.375n\varepsilon^2 \) at \( T \ll T_p \).

When concentration of impurities is equal to concentration of ‘basic’ ions \((n = 0.5)\) perturbation theory was compared with the exact calculations for the binary crystals. It is shown that both results are consistent and the difference is less than one per cent. The same order difference is between the perturbation theory and the linear mixing theory.

Obtained results indicate that the perturbation theory of the disordered crystal spectra developed by Lifshitz [6, 7] for terrestrial solids could be successfully used for crystals with isotopic impurities in neutron stars and white dwarfs. The difference between the heat capacity of ordered and disordered Coulomb crystals is small and does not play a noticeable role in the thermal evolution of degenerated stars.

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