Results for the energy of a finite one-dimensional ionic crystal

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We consider a one-dimensional ionic crystal consisting of an arbitrary number of alternating positive and negative ions. We calculate exactly the energy per ion and uncover some interesting patterns. It is found that the energy per ion remains constant each time the size of the system increases by one ion if addition of such an ion leads to a system with a nonzero total charge. On the other hand, the energy per ion always decreases if addition of such an ion leads to a charge neutral system with a zero total charge. Explicit analytical results are provided.

Keywords: Ionic crystal; Theory and modeling.

True one-dimensional (1D) ionic crystals are not easy to fabricate. Even apparently simple three-dimensional (3D) ionic crystals like $NaCl$ stay together in part because there are several types of long-range interactions that stabilize the system. Putting these ions along a 1D chain eliminates most of these interactions leading to the collapse of the 1D structure. However, recent advances in nanotechnology have made possible the fabrication of a stable 1D ionic crystal by trapping ions inside carbon nanotubes [1]. By tailoring the diameter of the carbon nanotubes to be slightly larger than that of selected ions, it was demonstrated that two chemical elements, one being a cation and the other an anion, align alternately inside carbon nanotubes [1]. The number of ions trapped along the carbon nanotubes can be arbitrarily chosen.

The simplest model considered would be a one-dimensional (1D) ionic crystal of an arbitrary number N (≥ 2) ions with alternating positive and negative charge, $\pm q$. The ions are localized in a 1D lattice with parameter, a. A pair of ions, i and j interact with a Coulomb electrostatic interaction of the form $U_{ij} = (\pm)\frac{k\,q^2}{r_{ij}}$ where the plus sign is for like (similar) charges and the minus sign for unlike (opposite) charges. The separation distance, r_{ij} is a positive integer multiple of a and k denotes Coulomb's electric constant. For the given model, the total (net) charge of the system, Q can be either zero if $N = 2, 4, 6, \ldots$ (even number) or $+q$ if $N = 3, 5, 7, \ldots$ (odd number). A schematic view of such a system of $N = 8$ ions is shown in Fig. 1.

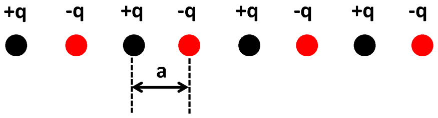

FIG. 1: Schematic view of a 1D ionic crystal consisting of $N = 8$ ions with alternating positive (solid circle - black) and negative (solid circle - red) charge.

The total energy of the 1D ionic crystal for an arbitrary number of ions, $N = 2, 3, \ldots$ can be written as:

$$U(N) = \sum_{i<j}^{N} U_{ij} = \frac{k\,q^2}{a} \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \frac{(-1)^{j-i}}{(j-i)} \; . \tag{1}$$

The energy per ion for a finite system of $N = 2, 3, \ldots$ ions is defined as:

$$\epsilon(N) = \frac{U(N)}{N} \; . \tag{2}$$

We initially thought that it is not possible to obtain exact analytical results for the energy of a system with an arbitrary number, N of ions. However, an analytic calculation of the energy per ion for systems with $2 \leq N \leq 15$ ions allowed us to uncover certain regular patterns that hinted otherwise. By using lengthy, though standard algebraic manipulations, we were able to prove analitically the following two important results that we report in this work:

$$\epsilon(N = 2\,n+1) = \epsilon(N = 2\,n) \quad ; \quad n = 1, 2, \ldots \tag{3}$$

and

$$\epsilon(N = 2\,n+2) = \epsilon(N = 2\,n+1) - \frac{1}{(2\,n+1)(2n+2)} \frac{k\,q^2}{a} \quad ; \quad n = 1, 2, \ldots \tag{4}$$

In Fig. 2 we show a plot of the energy per ion, $\epsilon(N) = U(N)/N$ (solid circles) as a function of N for systems with $2 \leq N \leq 15$ ions. Energies are expressed in units of $k\,q^2/a$. Note the emerging energy per ion pattern:

$$\epsilon(N=2) = \epsilon(N=3) \neq \epsilon(N=4) = \epsilon(N=5) \neq \epsilon(N=6) = \epsilon(N=7) \neq \ldots \tag{5}$$

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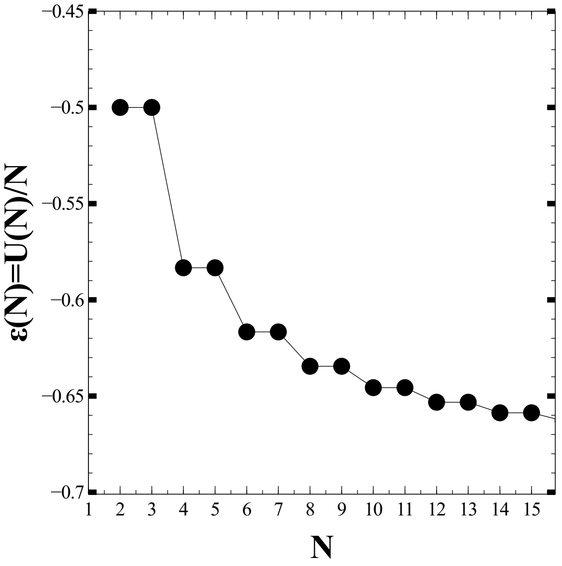

FIG. 2: Energy per ion, $\epsilon(N) = U(N)/N$ as a function of N for small values of $2 \leq N \leq 15$. The energy is given in units of $k\,q^2/a$. The solid line is a guide for the eye.

The proof of the results in Eq.(3) and Eq.(4), though lengthy, involves standard mathematical transformations. For instance, in order to prove the result in Eq.(3), one starts from the expression of the total energy of a system of $N = 2\,n + 1$ ions in terms of the total energy of a system of $N = 2\,n$ ions as follows:

$$U(2\,n+1) = U(2\,n) + \frac{k\,q^2}{a}\,S_{2\,n+1} \ , \tag{6}$$

where

$$S_{2\,n+1} = \sum_{i=1}^{2\,n} \frac{(-1)^{(2\,n+1-i)}}{(2\,n+1-i)} = \sum_{i=1}^{2\,n} \frac{(-1)^i}{i} \ , \tag{7}$$

and $n = 1, 2, \ldots$ is a positive integer. By noting that $1/(2n+1) = 1/(2n) - 1/[(2n)(2n+1)]$, one modifies Eq.(6) to write:

$$\frac{U(2n+1)}{2n+1} = \frac{U(2n)}{2n} + \frac{1}{2n+1}\left[\frac{k\,q^2}{a}\,S_{2n+1} - \frac{U(2n)}{2n}\right] \ . \tag{8}$$

With some care, on can prove/verify that $\sum_{i<j}^{2n}(-1)^{j-i}/(j-i) = (2n)\sum_{i=1}^{2n}(-1)^i/i$, which immeditely leads to:

$$\frac{U(2n)}{2n} = \frac{k\,q^2}{a}\,S_{2n+1} \ . \tag{9}$$

One obtains the formula in Eq.(3) by substituting the result from Eq.(9 into Eq.(8). The result in Eq.(4), though more challenging to derive, is proved by using a similar approach. The result in the thermodynamic limit is well-known [see page 64 of Ref. 2]:

$$\epsilon(N \to \infty) = -\ln(2)\,\frac{k\,q^2}{a} \ . \tag{10}$$

Note that our energy expression is per ion. It is customary in the literature [2] to calculate the energy per ion pair, rather than per ion. If there are N ions like in the current case, then there will be $N/2$ ion pairs. A reader can easily write all the results for the energy whichever way it prefers (either per ion, or per ion pair). Differently from the electron gas model where the overall charge neutrality of the system is guranteed by including a uniformly charged background [3–6], a 1D ionic crystal of the sort considered here has a built-in charge-neutrality in the thermodynamic limit.

To conclude, in this work we derived exact expressions [see Eq.(3) and Eq.(4)] for the energy of a finite 1D ionic crystal with an arbitrary number of ions. These results allow one to start from the simplest system with $N = 2$ ions and obtain the exact energy per ion at any arbitrary N with just a little bit of book-keeping. It is found that, each time we increase the size of the system by one ion, the energy per ion remains constant if addition of such an ion leads to a nonzero total charge. However, the energy per ion of the system always decreases if addition of such an ion makes the system charge neutral (the case when the system has an even N at the end). The peculiar dependence of the energy per ion as a function of the number of ions can be useful to experimental scientists since it appears to be a unique feature of this particular 1D model.

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