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Comment on "Correction to Fuchs' calculation of the electrostatic energy of a Wigner solid"

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It is found that Hall's correction term exactly cancels another electrostatic term in the total energy of the Wigner solid. Although Hall's correction is appropriate for the calculation of the potential at the Wigner lattice site, it is Fuchs' expression which should be used in the total electrostatic energy of the Wigner solid. The origin of the controversy is clarified using physical arguments, and a simpler derivation of Hall's term is presented.

In a recent paper, Hall[1] has argued that the widely used method of Fuchs[2] for calculating the electrostatic energy of a Wigner solid[3] contains an error. Hall finds a correction term which contributes about a 20% change to Fuchs' value, and more importantly, the magnitude of this term is structure dependent.

The present paper concludes that Hall's calculation of the electrostatic *potential* is correct, but there is another term in the total electrostatic *energy* of a solid which is not included in his calculation, and this term exactly cancels the proposed correction term. Since it is the total energy of the system which is to be compared in determining the relative stability of the Wigner lattice, Fuchs' original result is basically appropriate for calculations on solids.

The electrostatic energy of one point charge interacting with all other point charges and with the neutralizing uniform background of charge is, following Hall's conventions, given by

$$K \equiv q^2 {\sum_{\tau}^{\infty}}' \left(\frac{1}{\tau} - \frac{1}{\Omega}\int_{\tau}\frac{d^3r}{r}\right) - \frac{q^2}{\Omega}\int_0 \frac{d^3r}{r}, \tag{1}$$

where Ω is the volume per lattice point, q is the value of the point charge, and $\{\vec{\tau}\}$ is the Bravais lattice vector. The subscript 0 refers to the cell containing the origin. It has been shown that in the three-dimensional case

$$K = S + A, \tag{2}$$

$$S = q^2 \int_0^{\infty} \frac{1}{(\pi t)^{1/2}}\left[{\sum_{\tau}^{\infty}}' \exp(-t\tau^2) - \frac{1}{\Omega}\left(\frac{\pi}{t}\right)^{3/2}\right] dt, \tag{3}$$

$$A = \left(\frac{2\pi q^2}{3\Omega^2}\right)\int_0 r^2 d^3r. \tag{4}$$

S has been calculated for many crystal structures, and several equivalent expressions for S are available in the literature.[4] A has usually been neglected in the literature, and Hall refers to A as a "correction" term.

On the other hand, the total electrostatic energy of a Wigner solid per unit cell is

$$\begin{aligned}\gamma \equiv{}& \frac{q^2}{2}{\sum_{\tau}^{\infty}}'\left(\frac{1}{\tau} - \frac{1}{\Omega}\int_{\tau}\frac{d^3r}{r}\right) - \frac{q^2}{2\Omega}\int_0 \frac{d^3r}{r} \\ &+ \frac{q^2}{2\Omega}\int_0 \sum_{\vec{\tau}}^{\infty}\left(-\frac{1}{|\vec{\tau}-\vec{r}|} + \frac{1}{\Omega}\int_{\tau}\frac{d^3r'}{|\vec{r}-\vec{r}'|}\right) d^3r \\ ={}& \tfrac{1}{2}(K+B),\end{aligned} \tag{5}$$

$$B = \frac{q^2}{\Omega}\int_0 \sum_{\vec{\tau}}^{\infty}\left(-\frac{1}{|\vec{\tau}-\vec{r}|} + \frac{1}{\Omega}\int_{\tau}\frac{d^3r'}{|\vec{r}-\vec{r}'|}\right) d^3r. \tag{6}$$

$K/2$ contains the lattice-lattice interaction energy and one-half of the lattice-background interaction energy, whereas $B/2$ contains the remaining one-half of the lattice-background interaction energy and the background-background interaction energy. We have assumed that there is one atom per unit cell for simplicity, but generalization to many atoms or many kinds of atoms per unit cell is straightforward. Since Hall has evaluated K, the problem reduces to the calculation of B. We are now going to prove that $B = -A$, thereby establishing the following relation from Eqs. (2) and (5):

$$\gamma = \tfrac{1}{2}S. \tag{7}$$

The factor of one-half comes from the double counting of the electrostatic energy. In a momentum-space formalism for calculating the total energy of solids,[5] the above relation is implicitly assumed without proof. In Ref. 5, except for a pseudopotential contribution α_1, the electrostatic energy γ (which is called γ_{Ewald} in Ref. 5) is equated to $\frac{1}{2}S$.

A direct evaluation of integral B is difficult. Since B is the potential energy of the oppositely charged uniform background in the total potential field, it is convenient to express it as

$$B = -\frac{q}{\Omega}\int_0 \psi(\vec{r})\, d^3r. \tag{8}$$

Following Tosi's work,[6] the potential $\psi(\vec{r})$ is expressed as

$$\psi(\vec{r}) = \frac{4\pi q}{\Omega} \sum_{\vec{G}}{}' \frac{1}{G^2} \exp(-\eta^2 G^2/4 + i\vec{G}\cdot\vec{r}) + q \sum_{\vec{\tau}} \frac{1 - \mathrm{erf}(|\vec{r} - \vec{\tau}|/\eta)}{|\vec{r} - \vec{\tau}|} - \frac{q\pi\eta^2}{\Omega} + C\,, \tag{9}$$

where $\vec{G}$'s are reciprocal vectors, η is a parameter to be chosen to render fast convergence of the summation [$\psi(\vec{r})$ is independent of the choice of η], and C is the average potential which was neglected in Tosi's original work.[6] To prove that C is the average potential, we integrate $\psi(\vec{r})$ over the unit cell and divide it by Ω. The first summation in Eq. (9) gives zero contribution due to the $\exp(i\vec{G}\cdot\vec{r})$ factor. The second summation contributes $q\pi\eta^2/\Omega$ to the average potential, canceling the next term which was introduced for this purpose, and we then have

$$B = -qC\,. \tag{10}$$

To evaluate C, it is helpful to make a connection between $\psi(\vec{r})$ and K. K/q is, by definition, the potential at $\vec{r} = 0$ *without the point charge* q *at the origin*. Using Eq. (9), we get

$$\begin{aligned} K/q &= \frac{4\pi q}{\Omega} \sum_{G}{}' \frac{1}{G^2} \exp(-\eta^2 G^2/4) - q \lim_{r \to 0} \frac{\mathrm{erf}(r/\eta)}{r} + q \sum_{\tau}{}' \frac{1 - \mathrm{erf}(\tau/\eta)}{\tau} - \frac{q\pi\eta^2}{\Omega} + C \\ &= \frac{4\pi q}{\Omega} \sum_{G}{}' \frac{1}{G^2} \exp(-\eta^2 G^2/4) - \frac{2q}{\sqrt{\pi}\,\eta} + q \sum_{\tau}{}' \frac{1 - \mathrm{erf}(\tau/\eta)}{\tau} - \frac{q\pi\eta^2}{\Omega} + C\,. \end{aligned} \tag{11}$$

The first four terms on the right-hand side of Eq. (11) give another expression for S/q. For example, the expression by Coldwell-Horsfall and Maradudin[4] is obtained if we set $\eta = 1/\sqrt{\epsilon}$. Therefore we get

$$K = S + qC\,. \tag{12}$$

Combining Eqs. (2), (10), and (12), we finally get

$$B = -A\,, \tag{13}$$

thus proving our assertion.

Now the reason why A cancels in the total energy expression becomes clear. Since the system is neutral, the total energy is the difference between the potential felt by the point charge and by the uniform background. It is the relative potential at the lattice site with respect to the total average potential that contributes to the total energy. A constant shift of the potential does not affect the total energy.

It is *not* true, however, that the zero of the potential in the solid is arbitrary. Hall correctly calculated the absolute value of the potential. It is instructive to rederive his correction term in a simpler way with no less mathematical rigor. The only problem in the evaluation has been that the sums and the integrals cannot be interchanged when they do not converge properly. This problem can be avoided in the Fourier representation as employed by Tosi.[6] (This originated from Ewald[7] and Fuchs.[2]) In Eq. (9), the $\vec{G} = 0$ component of the total potential is left out in the summation, and a constant C is added. As C represents the average total potential, it should be identical to the $\vec{G} = 0$ component of the total potential in the periodic system. Callaway and Glasser[8] already noticed that this component is a well-defined quantity. Going back to the definition of the $\vec{G} = 0$ component of the total potential, we have

$$\begin{aligned} \lim_{G \to 0} \frac{1}{\Omega} \int_0 \frac{4\pi q}{G^2} \left(\delta(\vec{r}) - \frac{1}{\Omega}\right) \exp(i\vec{G}\cdot\vec{r})\, d^3r &= \lim_{G \to 0} \frac{4\pi q}{\Omega G^2} \int_0 \left(\delta(\vec{r}) - \frac{1}{\Omega}\right)\left(1 + i\vec{G}\cdot\vec{r} - \frac{(\vec{G}\cdot\vec{r})^2}{2}\right) d^3r \\ &= \lim_{G \to 0} \frac{4\pi q}{\Omega G^2}\left(1 - \frac{1}{\Omega}\int_0 d^3r - \frac{1}{\Omega}\int_0 i\vec{G}\cdot\vec{r}\, d^3r + \frac{G^2}{2\Omega}\int_0 \cos^2\theta\, r^2 d^3r\right) \\ &= \frac{2\pi q}{\Omega^2} \int_0 \cos^2\theta\, r^2 d^3r \\ &= C\,. \end{aligned} \tag{14}$$

The condition $\int \vec{G}\cdot\vec{r}\, d^3r = 0$ has been used in the above equation, since we always take the unit cell such that the dipole moment vanishes. For cubic structures, $\langle \cos^2\theta \rangle = \frac{1}{3}$, and we get Hall's result. For noncubic structures, C is not well defined as pointed out by Hall. However, following his prescription, it can be evaluated in a similar fashion.[1]

In the two-dimensional case, the correction term vanishes trivially because the Fourier representation has $1/G$ instead of $1/G^2$. More precisely, the average potential in the two-dimensional Wigner solid is, if σ is the unit area,

$$\lim_{G\to 0}\frac{1}{\sigma}\int_0 \frac{2\pi q}{G}\left(\delta(\vec{r})-\frac{1}{\sigma}\right)\exp(i\vec{G}\cdot\vec{r})d^2r$$
$$=\lim_{G\to 0}\frac{2\pi q}{\sigma G}\left(1-\frac{1}{\sigma}\int_0 d^2r-\frac{1}{\sigma}\int_0 i\vec{G}\cdot\vec{r}\,d^2r\right)$$
$$=0. \tag{15}$$

Physically, this happens because, contrary to the three-dimensional case, the quadrupole contribution of the region far from the origin vanishes.

In the one-dimensional case, the potential of the Wigner lattice diverges unless we define the uniform background (line charge) in a different way from higher-dimensional cases; therefore the correction term is not defined. Our method also provides a unique way of calculating the correction term in higher than three-dimensional cases, but we will not pursue this subject here.

Finally, is it possible to test our calculation ($B=-A$). Using a pseudopotential method, the total energy of Si for the bulk[9] and for the atomic limit[10] (very large lattice spacing) has been calculated by the authors, and the agreement with experiment is within 0.05 Ry per atom in each case. Since Hall's correction term would be on the order of 1 Ry in these cases, these results also suggest that the correction term should not enter the total energy.

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