Comments

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Comment on the average potential of a Wigner solid

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Ihm and Cohen have stated that it is *not* true that the zero of potential in a Wigner solid is arbitrary. We argue that it is arbitrary by demonstrating that the value obtained depends on how one performs a conditionally convergent Coulomb summation. We also derive the formula for the zero of energy in a semi-infinite crystal where it is a well-defined quantity.

In a recent paper Hall[1] claimed to have found a structure-dependent correction to Fuchs's formula [2] for the electrostatic energy of a Wigner solid. Both de Wette[3] and Ihm and Cohen[4] pointed out that Hall calculated the energy of an ion in the potential of the Wigner solid, that Hall's correction term was actually the contribution of the *average* potential to the energy of the ion, and that Hall neglected to add the exactly canceling contribution of the electrostatic energy of the background charge due to the average potential. Fuchs[2] took this average potential, which has usually been assumed to be completely arbitrary, to be zero. Ihm and Cohen[4] nevertheless state " It is *not* true, however, that the zero of the potential in the solid is arbitrary."

It is the purpose of this Comment to point out that because of the conditional nature[5] of the convergence of infinite Coulomb sums, the zero of potential in an infinite crystal is completely arbitrary. We also show how various ways of evaluating the sum (and thus obtaining different values for the average potential) correspond to different choices of the shape of the surface of the crystal before allowing the crystal to become infinite. We have previously discussed[6] how the Helmann-Feynman formula for the internal pressure in an infinite Wigner crystal yields a result depending on the shape of the surface, even though the internal pressure is actually a local quantity and therefore surface independent.

Let us first consider a neutral charge distribution $\rho(\vec{r})$ contained within a finite volume such that $\int \rho(\vec{r})d^3r=0$. Then

$$V(\vec{G}\to 0)=-\lim_{\vec{G}\to 0}\frac{1}{\Omega}\int\frac{4\pi}{G^2}\rho(\vec{r})e^{i\vec{G}\cdot\vec{r}}d^3r$$
$$=-\lim_{\vec{G}\to 0}\frac{4\pi}{G^2}\left[\int\rho(\vec{r})d^3r+iG\int r\rho(\vec{r})\cos\theta\, d^3r-\tfrac{1}{2}G^2\int r^2\rho(\vec{r})\cos^2\theta\, d^3r\right]$$
$$=\lim_{\vec{G}\to 0}\frac{4\pi}{\Omega}\left[\frac{-i}{G}\int r\rho(\vec{r})\cos\theta\, d^3r+\tfrac{1}{2}\int r^2\rho(\vec{r})\cos^2\theta\, d^3r\right]. \quad (1)$$

If $\rho(\vec{r})$ has spherical or cubic symmetry about the point charge

$$V_{\text{cubic}}(\vec{G}\to 0)=\frac{2\pi}{3\Omega}\int r^2\rho(\vec{r})d^3r\,. \quad (2)$$

Here Ω is an arbitrary volume which we will later identify with a unit cell. Note that in general $V(\vec{G}\to 0)$ depends through the $\cos\theta$ on the direction from which $\vec{G}$ approaches zero. Even in the cubic case $V(\vec{G}=0)$ is not defined by this limiting procedure because $\int\rho(\vec{r})d^3r\,G^{-2}$ and $\int\cos\theta\, d\Omega\, G^{-1}$ are not defined for $G=0$. To obtain $V(\vec{G}=0)$ we evaluate

$$V(0)=-\frac{1}{\Omega}\int\int\frac{\rho(\vec{r}')}{|\vec{r}-\vec{r}'|}d^3r'd^3r$$

$$=\frac{-2\pi}{\Omega}\int\int\int\rho(\vec{r}')(r^2+r'^2-2rr'\cos\theta)^{-1/2}\times\sin\theta\,d\theta\,r^2dr\,d^3r'$$

$$=\frac{-4\pi}{\Omega}\int\int\rho(\vec{r}')\frac{1}{r_>}r^2dr\,d^3r'$$

$$=\frac{2\pi}{3\Omega}\int\rho(\vec{r}')r'^2d^3r' . \quad (3)$$

In order to obtain this result we had to fix the arbitrary additive constant by choosing $V(r\to\infty)=0$. The change in the order of integration is justified by noting that the $\vec{r}'$ integration vanishes outside a sphere containing all the charge; the integration over $\vec{r}$ also vanishes outside the sphere if the angular integration is performed before the radial providing we restrict ourselves to charge distributions with no net dipole.[7]

The average potential in a finite crystal with identical unit cells is

$$V_{\text{cryst}}(0)=-\frac{1}{N\Omega}\sum_{i=1}^{N}\int\int\frac{\rho_i(\vec{r}'-\vec{r}_i)}{|\vec{r}-\vec{r}'|}d^3r'd^3r$$

$$=\frac{2\pi}{3\Omega}\int\rho_i(\vec{r}'-\vec{r}_i)r'^2d^3r' , \quad (4)$$

where $\rho_i(\vec{r}-\vec{r}_i)$ is the charge associated with the ith unit cell and $\vec{r}_i$ is an arbitrary origin for the ith unit cell. Note that if we restrict ourselves to a Wigner crystal where

$$\rho_i(\vec{r}-\vec{r}_i)=q[\delta(\vec{r}-\vec{r}_i)-\Omega^{-1}] ,$$

then $-qV_{\text{cryst}}(0)$ becomes identical to the "correction term" obtained in a very complicated derivation by Hall[5] for noncubic crystals. It is obviously also valid for cubic crystals whether or not the unit cells are chosen to be cubic. Note also that Eq. (4) says that the correct generalization of Ihm and Cohen's formula for cubic cells is to make a spherical average over all the directions from which $\vec{G}$ may approach zero. One is free to choose the $\rho_i(\vec{r}'-\vec{r}_i)$ in an infinite number of ways, the only restriction being that

$$\sum_i\rho_i(\vec{r}'-\vec{r}_i)=\rho_{\text{cryst}}(\vec{r}') .$$

The $\rho_i(\vec{r}'-\vec{r}_i)$ may overlap or each may be restricted to its own unit cell. In the latter case, there are an infinite number of choices one may make for the unit cell. Each choice of overlapping ρ's or unit cells for nonoverlapping ρ's yields a different surface charge distribution and it is this that makes $V_{\text{cryst}}(0)$ dependent on that choice. For example, the proximity cell chosen by Hall yields a waffled surface whereas slab-adapted unit cells[8] yield a smooth surface. Although neither cell has a dipole, the difference between two Wigner crystals made up from these two kinds of cells is a surface double layer. Because N may be allowed to be infinite in Eq. (4), the infinite crystal, which has no surface, has an arbitrary average potential, depending on the surface assumed in the limiting process. In allowing N to become infinite one must require that all components of $\vec{r}_N$ become infinite together. If one or two dimensions of the crystal are taken to be infinite and the remaining dimension(s) is either finite or approaches infinity, Eq. (4) is not valid because the reversal in the order of the $\vec{r}'$ and $\vec{r}$ integrations used to derive it, is invalid.

The average potential in a semi-infinite crystal is well defined and physically meaningful. The planar average of the potential within any slab-adapted unit cell of area A and thickness $2L$ is

$$V_0(z)=\frac{2\pi}{A}\int_{-L}^{L}|z-z'|\rho(z')dz' . \quad (5)$$

This represents the potential from the planar average of the charge within an infinite slab of thickness $2L$. Because each slab contains no net charge, after the planar averaging there are no contributions to the potential in one slab from its neighboring slabs. Thus Eq. (5) represents the planar average of the Coulomb potential anywhere within the semi-infinite crystal,[9] except for corrections due to deviations of the charge in the surface unit cells from its bulk value.

We now average over z to obtain.

$$V_{\text{slab}}(0)=\frac{2\pi}{2LA}\int_{-L}^{L}dz\left[\int_{-L}^{z}(z-z')\rho(z')dz'-\int_{z}^{L}(z-z')\rho(z')dz'\right]$$

$$=\frac{2\pi}{\Omega}\int_{-L}^{L}dz'\rho(z')\left[\int_{z'}^{L}(z-z')dz-\int_{-L}^{z'}(z-z')dz\right]=\frac{2\pi}{\Omega}\int_{-L}^{L}\rho(z')z'^2dz' , \quad (6)$$

where we have used $\int_{-L}^{L} \rho(z')dz' = 0$ in the last step. As might have been expected, this result is identical to that obtained from Eq. (1) if $\vec{G} \to 0$ from the surface normal direction so that $r^2\cos^2\theta = z^2$ and if $\rho(\vec{r})$ is taken to be the charge within a slab-adapted unit cell. It should perhaps be pointed out that this definition of the average potential leads to the correct work function and that so long as the crystal is taken to be infinite in the plane before being allowed to become semi-infinite in the normal direction, the work function is independent of the shape of the unit cell chosen. This is because the surface charge is a well-defined quantity and the surface charge correction term corrects the charge obtained from a superposition of bulk unit-cell charges.

In conclusion, the average potential in an infinite crystal which has no surface is a meaningless quantity because it depends on the surface chosen before the crystal was allowed to become infinite whereas the average potential for a semi-infinite crystal is a perfectly well-defined quantity which differs from the infinite crystal result of Eq. (4) no matter what shape unit cell is inserted into that equation.

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[1]G. L. Hall, Phys. Rev. B 19, 3921 (1979).
[2]K. Fuchs, Proc. R. Soc. London 151, 585 (1935).
[3]F. W. de Wette, Phys. Rev. B 21, 3751 (1980).
[4]J. Ihm and M. L. Cohen, Phys. Rev. B 21, 3754 (1980).
[5]Hall recognized that his "correction term" was conditionally convergent but appeared to believe that a particular prescription for performing the sum led to a physically meaningful result.
[6]L. Kleinman, Phys. Rev. B 3, 3083 (1971).
[7]If the unit cell has a net dipole, the value of $V(0)$ obtained from Eq. (3) depends on the origin chosen. The reversal of the order of integration is not valid in the dipole case because the integral of $1/r$ is infinite. If the unit cell has a quadrapole moment, the radial infinity is sufficiently weak that the integration over $\vec{r}$ does vanish outside the sphere.
[8]One may choose a slab-adapted unit cell for any of the infinite number of Miller-index surfaces. By slab-adapted unit cell we mean a cell whose base is the cell for the two-dimensional surface plane of the slab and whose perpendicular dimension is taken to give the cell the correct volume (for primitive lattices this is just the interplanar spacing).
[9]It also represents the planar average of the potential in an infinite crystal as long as one takes the crystal to be infinite in the plane and then approach infinity in the normal direction.