Surface Stress of Point Charge Lattices

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In surface science it is quite a common problem to want to know the electrostatic potential near the surface of a crystal or ionic liquid. ¿From a modelling point of view, the surface is usually represented by a two-dimensionally repeating unit cell of charges. The $2D$ vector, $\underline{n}$, denoting the position of the unit cell is given by,

$$\underline{n} = i\hat{x}L_x + j\hat{y}L_y, \tag{1}$$

where the unit vectors $\hat{\gamma}$ are along the $\underline{\gamma}$ direction, the corresponding cell sidelengths are, L_γ and the integers i, j range over $0, \pm 1, \pm 2, \cdots, \pm\infty$. The x and y directions form the surface plane. The z direction is perpendicular to the surface plane. Consider N point charges of index i with point charge values, q_i in a unit cell of volume, V. These charges are positioned at $r_{\underline{n}i}$ where $1 \leq i \leq N$ and $\underline{n}$ indicates the lattice cell in which it is found. A semi-infinite or 'half-space' is built up from a series of these laminae positioned parallel and packed together.

The total coulomb interaction energy, Φ of the point charge system is,

$$2\Phi = \sum_{i=1}^{N}\sum_{j=1}^{N}\sum_{\underline{n}} q_i q_j r_{\underline{n}ij}^{-1}, \tag{2}$$

where $r_{\underline{n}ij} = \mid \underline{r}_{\underline{n}ij} \mid = \mid \underline{r}_{\underline{n}i} - \underline{r}_{\underline{n}j} \mid$. There is a null entry in equation 2 for $i = j$ when $\underline{n} = 0$.

For a bulk point charge lattice, Ewald recast this summation as two series, one in real space and the other in Fourier space (covering the reciprocal lattice). Both of these series can be caused to converge rapidly by a suitable choice of an arbitrary parameter, κ, present in both series. An analoguous procedure was followed by Parry [1] [2] for laminar and semi-infinite geometries. We have,

$$\begin{aligned} 2\Phi &= \frac{\sum_{i=1}^{N}\sum_{j=1}^{N}\sum_{\underline{n}}^{\infty} q_i q_j erfc(\kappa r_{\underline{n}ij})}{r_{\underline{n}ij}} \\ &+ \frac{\pi}{A}\sum_{\underline{h}}^{\infty}\sum_{i=1}^{N} q_i \sum_{j=1}^{N} q_j F(\kappa, \underline{h}, r_{zij})\Re[\exp(i\underline{h}.\underline{r}_{ij})] - \sum_{i=1}^{N}\frac{2\kappa q_i^2}{\pi^{1/2}}, \end{aligned} \tag{3}$$

where $erfc(\cdots)$ is the complementary error function, r_{zij} is the z or 'out-of-plane' component of $r_{\underline{n}ij}$ (the same for all $\underline{n}$) and $\Re$ denotes the real part of the complex quantity. The original summation of equation 2 is carried out in real space; however, in equation 3 this is transformed into two summations, one in real space (over the same real space lattice, $\underline{n}$) and one in reciprocal space (over the reciprocal lattice, $\underline{h}$). The quantity, κ is an adjustable parameter with units of inverse length. The value of κ determines the relative emphasis given to the real and reciprocal space terms; the reciprocal space series increasingly dominates in contribution as κ increases. The in-plane area of the unit cell, A, equals, $A = |\underline{L}_x \times \underline{L}_y|$. The reciprocal lattice vector is defined by,

$$\underline{h} = 2\pi(i\hat{x}/L_x + j\hat{y}/L_y). \tag{4}$$

Also,

$$F(\kappa, \underline{h}, r_{zij}) = (\exp(hr_{zij})erfc(h/2\kappa + r_{zij}\kappa) + \exp(-hr_{zij})erfc(h/2\kappa - r_{zij}\kappa))h^{-1}, \tag{5}$$

for $h \neq 0$ and,

$$F(\kappa, \underline{h} = 0, r_{zij}) = -2[r_{zij}erf(r_{zij}\kappa) + \exp(-(r_{zij}\kappa)^2)/\kappa\pi^{1/2}], \tag{6}$$

for $h = 0$.

The purpose of the talk was to show how the Parry formulae could be developed further to obtain the components of the stress tensor [3]. For example, the coulombic component of the stress tensor (including both real and reciprocal space series) for the xx, xy, yx and yy components is given by,

$$\begin{aligned} -S_{\alpha\beta}V &= \sum_{i=1}^{N} q_i \sum_{j=1}^{N} q_j \sum_{\underline{n}}^{\infty} \frac{1}{2}\left(\frac{2}{\sqrt{\pi}}\kappa r_{\underline{n}ij}\exp(-\kappa^2 r_{\underline{n}ij}^2) + erfc(\kappa r_{\underline{n}ij})\right)\frac{r_{\alpha\underline{n}ij} r_{\beta\underline{n}ij}}{r_{\underline{n}ij}^3} \\ &+ \frac{\pi}{2A}\sum_{\underline{h}}^{\infty}\sum_{i=1}^{N} q_i \sum_{j=1}^{N} q_j B_{\alpha\beta}\Re[\exp(i\underline{h}.\underline{r}_{ij})], \end{aligned} \tag{7}$$

where for $h \neq 0$,

$$B_{\alpha\beta} = \delta_{\alpha\beta} F(\kappa, \underline{h}, r_{zij}) + h_\alpha h_\beta h^{-2} \{ (r_{zij} - h^{-1}) \exp(h r_{zij}) erfc(h/2\kappa + r_{zij}\kappa) - (r_{zij} + h^{-1}) \exp(-h r_{zij}) erfc(h/2\kappa - r_{zij}\kappa) - \exp(h r_{zij}) \exp(-(h/2\kappa + r_{zij}\kappa)^2)/\kappa\pi^{1/2} - \exp(-h r_{zij}) \exp(-(h/2\kappa - r_{zij}\kappa)^2)/\kappa\pi^{1/2} \} \quad (8)$$

where $\delta_{\alpha\beta}$ is the Kronecker delta. For, $h = 0$ we have,

$$B_{\alpha\beta} = \delta_{\alpha\beta} F(\kappa, \underline{h} = 0, r_{zij}). \quad (9)$$

References

[1] D.E. Parry, Surface Sci. 49 (1975) 433; 54 (1976) 195.

[2] D.M. Heyes, Surface Sci. 110 (1981) L619.

[3] D.M. Heyes, Surface Sci. in press (1993).