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On the determination of defect dipoles from atomistic simulations using periodic boundary conditions

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ABSTRACT

By solving the problem of a periodic distribution of point defects in general anisotropic media, we give an alternative, more direct proof, of the relatively recent procedure that extracts dipole tensors from the stress acting on the cell of atomistic simulations performed under periodic boundary conditions. Moreover, we show that naive superposition of individual defect fields is not a solution of the problem, though correction terms can be identified; as a byproduct, analysis of the latter allows us to reveal a spurious contribution to the elastic interaction energy as calculated in current literature procedures, that therefore must be subtracted in order to obtain correct results.

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Within the context of continuum elasticity theory, point defects are modelled through the concept of dipole (or double force) tensor (see e.g. [1]): a set of three perpendicular, opposite force couples, possessing zero resultant and torque, that fully determines the displacement field. Experimentally, techniques such as the diffuse scattering of X-rays [2] can be employed to measure those long-range fields, so that invaluable information on defect structure at a fundamental level may be obtained. Since the rather early computer simulations of the 1960s, simplified versions of the dipole were used to self-consistently adjust the position of atoms at the super-cell boundary [3], thus improving the reliability of the simulations and optimizing the computing resources then available. Approaches of this sort, however, were rather biased towards simulations involving dislocations [4], where application of the elastic field to the boundary atoms is intrinsic to the defect. The calculation of point defect dipoles from atomistic simulations, was put in a more or less definitive form by Schober and Ingle [5], who devised a methodology based on the forces on the boundary atoms, fixed at their perfect lattice positions, that arise after static relaxation of the defect. The aim was to determine the dipoles themselves, rather than improving simulations, either as a predictive tool to aid experiment or as a test for the force laws proposed. In the latter sense, for instance, the present authors [6] had worked out a generalization of early ideas by Kanzaki [7], that allows to estimate the size of the anharmonic region around a point defect.

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All of the previous simulations were static in nature and employed finite super-cells. Closer in time, with the popularization and widespread availability of atomistic codes implementing both, classic molecular dynamics and electronic structure theory via Density Functional Theory (DFT), periodic boundary conditions (PBC) have become the de facto choice. However, until very recently, the problem of evaluating defect dipoles under PBC remained basically unexplored, partially because of the flexible cell methods (such as Parrinello and Rahman's [8]) included in most codes, that allow immediate access to the volume change induced by defects (one motivation to compute dipoles). Renewed interest came from the DFT simulation of self-interstitials structure, mainly in connection with the technologically important metal Zr [9]. Here, the marked structure polymorphism and the limited size of feasible super-cells (order of 100 atoms), rendered the problem of finding the most stable configuration virtually impossible. Differences among simulations performed using rigid cells, flexible cells, or the in-between approach proposed in [10], shed doubts on the reliability of the results. The issue has been finally cleared by Varvenne et al. [11] who, by applying elastic dipole–dipole interaction corrections, were able to obtain consistent results, independent on the way the cell is handled, as long as it is larger than a minimum size. (Before continuing, we'd like to remark that the above succinct account is only meant to set the scene, no claims to have done justice to the large body of literature for such an aged subject are made.)

Those corrections rely on determining the dipole tensor directly from the residual stress present in the (periodic) cell after static relaxation of the defect. The argument in support of this procedure [12] is rather indirect: firstly, the minimum energy, zero stress, condition reached by static relaxation with a flexible cell is identified, secondly, the dipole is extracted from the (elastic) work done as the cell is uniformly strained back in order to reach its starting size and shape. Besides, those corrections also involve a conditionally convergent sum over all periodic images of the reference cell, that the authors handled via the technique proposed in [13]. Here, we offer a more direct proof of the procedure to extract the dipole, based on solving for the displacement field that stems from a periodic distribution of point defects in a general anisotropic medium. Moreover, we show that naive superposition of individual defect fields is not a solution of the problem; however, correction terms can be identified, and from them we are able to derive an expression representing a correction to the elastic interaction energy, as currently practiced in the literature.

Our point of departure is the relationship (see e.g. [14] p.147),

$$-\int_S \vec{T}\otimes\vec{x}\,\mathrm{d}S+\int_\Omega \bar{\bar{\sigma}}\,\mathrm{d}\tau=\int_\Omega \vec{f}\otimes\vec{x}\,\mathrm{d}\tau\equiv\bar{\bar{P}}\,, \tag{1}$$

derived by applying Gauss' theorem to the static equilibrium equations for the stress, $\bar{\bar{\sigma}}$, acting on an elastic body of volume Ω, bounded by a surface S, and loaded with volume forces of density $\vec{f}$. Here, $\otimes$ stands for tensor product, $\vec{x}$ for position, $T_i \equiv \sigma_{ij}n_j$ is the surface traction, and $\bar{\bar{P}}$ is (by definition) the defect dipole. If the bounding surface is free, tractions are zero, which leads to,

$$\int_\Omega \bar{\bar{\sigma}}\,\mathrm{d}\tau=\bar{\bar{P}}\quad(\vec{T}=0), \tag{2}$$

apparently in contradiction to the relationship,

$$-\Omega\langle\bar{\bar{\sigma}}\rangle = \bar{\bar{P}}, \tag{3}$$

used in the simulations to obtain the defect dipole from the computed stress acting on the cell (now of volume Ω and surface area S). This is however a deceiving conclusion. For an infinite periodic array of defects, the displacement field, $\vec{u}(\vec{x})$, must possess the periodicity implied by the cell; thus, considering its Fourier's expansion and the fact that stress is given in terms of displacement derivatives, one must have $\int_\Omega \bar{\bar{\sigma}}\, \mathrm{d}\tau = 0$, so that under rigid cell PBC, Equation (1) takes the form,

$$-\int_S \vec{T} \otimes \vec{x}\, \mathrm{d}S = \bar{\bar{P}} \quad (\langle\bar{\bar{\epsilon}}\rangle = 0). \tag{4}$$

The above indeed coincides with Equation (3), after realizing that the atomistic stress calculated for a relaxed configuration, comes from the work, $\mathrm{d}U$, done by the forces crossing the boundary of the cell as the latter is distorted by a small (arbitrary) strain, $\delta\bar{\bar{\epsilon}}$, namely,

$$\Omega\langle\bar{\bar{\sigma}}\rangle \,:\, \delta\bar{\bar{\epsilon}} \equiv \mathrm{d}U = \int_S \mathrm{d}S\, \vec{T}.\delta\bar{\bar{\epsilon}}.\vec{x} = \delta\bar{\bar{\epsilon}} : \int_S \mathrm{d}S\, \vec{T} \otimes \vec{x}\,, \tag{5}$$

(note $\delta\vec{u} = \delta\bar{\bar{\epsilon}}.\vec{x}$ here, and that dot and colon stand for the mathematical contraction of one and two indexes respectively).

We turn now to obtaining an explicit representation for the displacement field of the elastic problem, and effectively show that Equation (4) is fulfilled. The equations to be solved are then,

$$C_{jkil}\, \frac{\partial^2 u_i(\vec{x})}{\partial x_k \partial x_l} = -\sum_n f_j(\vec{x} - \vec{l}_n)\,, \tag{6}$$

where C_{jkil} is the tensor of elastic constants, and the right-hand side is a distribution of forces centred about the origin and its periodic images ($\vec{l}_n$ stand for lattice vectors, repeated index summation implied). Under these conditions, all functions must be Fourier's expandable in terms of reciprocal lattice vectors $\vec{K}$, so that the PBC are automatically built in, therefore,

$$u_i(\vec{K}) = \frac{M^*_{ij}(\hat{\boldsymbol{K}})}{K^2} f_j(\vec{K}) \tag{7a}$$

$$f_j(\vec{K}) = \int_\Omega \sum_n f_j(\vec{x} - \vec{l}_n) \exp\{-i\vec{K}.\vec{x}\}\, \mathrm{d}\vec{x} = \int_{-\infty}^{+\infty} f_j(\vec{x}) \exp\{-i\vec{K}.\vec{x}\}\, \mathrm{d}\vec{x} \tag{7b}$$

$$\therefore \quad u_i(\vec{x}) = \frac{1}{\Omega} \sum_{\vec{K}\neq 0} u_i(\vec{K})\ \exp\{i\vec{K}.\vec{x}\} \tag{7c}$$

The term $\vec{K} = 0$ is omitted because forces have zero resultant, M^*_{ij} is the inverse of matrix $C_{jkil}\hat{K}_k\hat{K}_l$ (see e.g. [15]), and the hat accent indicates vectors of unit length. In the limit of point-like dipoles, the exp{} function entering $f_j(\vec{K})$ can be expanded about the origin leading to,

$$f_j(\vec{K}) \approx -iK_k \int f_j(\vec{x})\, x_k\, \mathrm{d}\vec{x} \equiv -iK_k\, P_{jk}\,; \tag{8}$$

this assumption is convenient and enough for our present purposes, though not strictly needed for the validity of the results. Thus, after noticing displacements are real, Equation (7c) may be rewritten as,

$$u_i(\vec{x}) = \frac{1}{\Omega} \sum_{\vec{K}\neq 0} \frac{M^*_{ij}(\hat{\boldsymbol{K}})}{K} \hat{K}_k \, \sin(\vec{K}.\vec{x}) \quad P_{jk} \, . \tag{9}$$

To establish contact with Equation (4), which left-hand side integral will be termed $\bar{\bar{\Pi}}$ for short, the above is transformed to strain and then contracted with the elastic constant tensor, so that,

$$\Pi_{mt} = -\frac{P_{jk}}{\Omega} \sum_{\vec{K}\neq 0} C_{mnil} \, M^*_{ij}(\hat{\boldsymbol{K}}) \, \hat{K}_k \, \hat{K}_l \int_S \mathrm{d}S \hat{K}^S_n x^S_t \cos(\vec{K}.\vec{x}^S) \tag{10}$$

where the superscript S indicates a point on the faces of the cell parallelepiped, and $\hat{K}^S_n$ is the outer perpendicular to each face. The integral on the right is decomposed in pairs of parallel faces (and opposite normals), noting the points, $\vec{x}^S$ and $(\vec{x}^S + \vec{a}^S)$, associated through the cell edge, $\vec{a}^S$, where the cosine takes the same value; therefore,

$$\int_S \mathrm{d}S \hat{K}^S_n x^S_t \cos(\vec{K}.\vec{x}^S) = \sum_{S=1}^{S=3} \int_S \mathrm{d}S \hat{K}^S_n a^S_t \cos(\vec{K}.\vec{x}^S) \, . \tag{11}$$

Due to the cosine periodicity, the above selects only the $\vec{K}$ vectors perpendicular to the faces, then the integral evaluates trivially to $\hat{K}^S_n \, a^S_t \, A^S \cos(\vec{K}^S.\vec{x}^S_0)$, being $\vec{x}^S_0$ a point on the face and A^S its area. Moreover, after noting that $C_{mnil}\hat{K}_n\hat{K}_l \; M^*_{ij} = \delta_{mj}$, Equation (10) is reduced to,

$$\Pi_{mt} = -\frac{P_{mj}}{\Omega} \sum_{S=1}^{S=3} A^S a^S_t \hat{K}^S_j \sum_{\vec{K}^S\neq 0} \cos(\vec{K}^S.\vec{x}^S_0) \, . \tag{12}$$

Because of the condition on $\vec{K}^S$, the cosine's argument takes values that are integer multiples of some angle, $\nu \, \phi^S_0$; thus we add and subtract the term for $\nu = 0$, and note that the so completed sum evaluates to zero, for symmetry reasons. The sought for result $\Pi_{mt} = P_{mt}$ follows immediately after the identity (relationship between reciprocal cells),

$$\frac{1}{\Omega} \sum_{S=1}^{S=3} A^S a^S_t \hat{K}^S_j = \delta_{jt} \, . \tag{13}$$

In the last part of the article we analyse the problem from the point of view of individual defect fields. In particular, it is worth noticing that the concept of elastic interaction between defects, can hardly be defined within the previous approach, because displacements do not recognize contributions from the different images; lattice information enters only through reciprocal vectors. An example suffices to convince oneself that a naive superposition of displacements cannot be a solution to the problem of Equation (6). A correct solution must not change the cell's volume; then imagine a lattice of isotropic defects embedded

in an isotropic medium, for which it is well known [1] that displacement fields behave as $\sim \hat{r}/r^2$, where r is the distance to the sources. Considering a reference cell, it is also known that the defect it contains entails a volume change, which cannot be countered by the fields of the images, because the previous form possesses zero divergence. Thus we hit a contradiction. Pictorially, as soon as the field of the defects is turned on, the periodic cell undergoes a uniform strain; the lattice still remains periodic but with a changed unit cell. This virtual strain can be calculated rather easily. First, notice that the sum in Equation (7c) is now replaced by an integral in reciprocal space, $\sum_{\vec{K}} \rightarrow \Omega/8\pi^3 \int \mathrm{d}\vec{k}$; second, consider the following strain integral (point-like defect model assumed),

$$E_{il} \equiv \int \epsilon_{il}\,\mathrm{d}\tau = \frac{1}{8\pi^3} P_{jk} \int_{\phi_1} \sin\theta_1 \mathrm{d}\theta_1 \mathrm{d}\varphi_1\, \hat{k}_k \hat{k}_l\, M^*_{ij}(\hat{\boldsymbol{k}})\, J(\hat{\boldsymbol{k}})\ , \tag{14}$$

with,

$$J(\hat{\boldsymbol{k}}) \equiv \int_0^\infty k^2 \mathrm{d}k \int_0^\infty r^2 \mathrm{d}r \int_{\phi_2} \sin\theta_2 \mathrm{d}\theta_2 \mathrm{d}\varphi_2\ \cos\left(k\, r\, \hat{\boldsymbol{k}}.\hat{\boldsymbol{r}}\right)\ , \tag{15}$$

where an isolated defect is located at the centre of a large sphere, and ϕ_i stand for spheres of unit radius. Calculation of $J(\hat{\boldsymbol{k}})$ needs some care and it is postponed till the Appendix 1, where we show it equals $2\pi^2$. Because the above is shared among all the cells of the lattice and there is one defect per cell, the referred strain amounts to $\langle\bar{\bar{\epsilon}}\rangle = \bar{\bar{E}}/\Omega$. Moreover, this impacts the summed elastic interaction energy of a given defect with all its images by adding an extra self-term given by,

$$U_{SLF} = \frac{1}{2} P_{il} \frac{E_{il}}{\Omega} = \frac{1}{2\,\Omega} P_{il} P_{jk}\ \langle \hat{k}_k \hat{k}_l\, M^*_{ij}(\hat{\boldsymbol{k}})\rangle_{\phi_1}\ , \tag{16}$$

where $\langle . \rangle_{\phi_1}$ stands for average on the unit sphere, and the factor 1/2 accounts for the fact that $\bar{\bar{P}}$ and $\bar{\bar{E}}$ stem from the same source. Again, the case of pure dilation centres embedded in isotropic media is illustrative. As is well known, their interaction energy is zero; however, calculations with tools from the literature ([11], supplementary material) obtain values that match those from Equation (16) but for numerical errors. In other words, for correct results Equation (16) must be subtracted, and to obtain the total correction (to be subtracted) for the defect formation energy, E^f, a term $\bar{\bar{P}} : \langle\bar{\bar{\epsilon}}\rangle - 1/2\ \Omega\langle\bar{\bar{\epsilon}}\rangle : C : \langle\bar{\bar{\epsilon}}\rangle$ must be added back, accounting for the cell strain $\langle\bar{\bar{\epsilon}}\rangle$ that would otherwise take place if not hindered by the PBC. Interestingly, in the special case of both, defect and medium, being isotropic, such a non-null result comes fully from the so-called aperiodic correction for conditionally convergent lattice sums introduced in [13]. A further representative example is reported in Table 1 for the case of standard self-interstitial configurations in Zr and Zn, from simulations performed by the authors [16], using rigid hexagonal cells comprising 96 sites ($4 \times 4 \times 3$). The values correspond to the total elastic correction and its partial interaction contribution, to be subtracted from the bare defect formation energy, in order to account for PBC effects. The Zr example is particularly relevant because it has been shown that a reliable prediction of formation energies and their relative ordering, requires larger than 96 sites cells [11,17,18]. The issue chiefly involves configurations Bo, Bs and O, the current consensus being E^f (Bo) < E^f (Bs) < E^f (O); in any case, our results from Table 1, though more precise than previous approaches [11], are unlikely to change that conclusion. The example of Zn is less critical in this sense; from our current perspective its

Table 1. Elastic correction (to be subtracted, meV rounded) to the formation energy of typical self-interstitial configurations in Zr and Zn; interaction component on the right. See main text for details.

Metal	O	Bo	C	S	Bs
Zr	118/8	165/48	125/8	145/21	218/77
Zn	205/−6	570/194	188/−13	224/2	764/288

interest resides in showing that what in principle would be taken as a repulsive interaction between defects, might turn into attractive after consideration of Equation (16), most likely due the enhanced anisotropy of Zn as compared to Zr.

Two closing remarks are worth mentioning; firstly, for stronger defects such as clusters, dislocation dipoles, inclusions, etc., the size of the elastic interaction becomes more important than Table 1 may suggest, notice the P^2 dependence; secondly, the analyses around Equation (14) and its consequence Equation (16), apply generally, not only to point defects.

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Disclosure statement

No potential conflict of interest was reported by the author.

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Appendix 1. Evaluation of Equation (15)

We start by performing the integral over ϕ_2 (z-axis aligned with $\hat{\boldsymbol{k}}$),

$$J(\hat{\boldsymbol{k}}) = 4\pi \int_0^\infty k\mathrm{d}k \int_0^\infty r\mathrm{d}r \, \sin(kr) \,, \tag{A1}$$

the dependence on $\hat{\boldsymbol{k}}$ is then gone, so that just J will be written in what follows. The above is interpreted as an integral on the first quadrant, thus by switching to polar coordinates, $k = \rho \sin\theta$, $r = \rho\cos\theta$, $\sin\theta\,\cos\theta = \frac{1}{2}\sin 2\theta$, and setting $2\theta = \varphi$, one obtains,

$$\begin{aligned} J &= 2\pi \int_0^\infty \rho^3 \mathrm{d}\rho \int_0^\pi \mathrm{d}\varphi \, \frac{\sin\varphi}{2} \, \sin\left(\rho^2 \frac{\sin\varphi}{2}\right) \\ &= 2\pi \int_0^\infty \rho\mathrm{d}\rho \int_0^\pi \mathrm{d}\varphi \, \tan\varphi \, \frac{\rho^2\cos\varphi}{2} \, \sin\left(\rho^2 \frac{\sin\varphi}{2}\right) . \end{aligned} \tag{A2}$$

After integrating by parts on φ,

$$\begin{aligned} J &= 2\pi \int_0^\infty \rho\mathrm{d}\rho \int_0^\pi \mathrm{d}\varphi \, \frac{1}{\cos^2\varphi} \, \cos\left(\rho^2 \frac{\sin\varphi}{2}\right) \\ &= 2\pi \int_0^\pi \mathrm{d}\varphi \, \frac{1}{\cos^2\varphi} \int_0^\infty \rho\mathrm{d}\rho \, \cos\left(\rho^2 \frac{\sin\varphi}{2}\right) \\ &= 2\pi^2 \int_0^\pi \frac{1}{\cos^3\varphi} \, \delta(\sin\varphi) \, \cos\varphi \, \mathrm{d}\varphi \\ &= 2\pi^2 \,, \end{aligned} \tag{A3}$$

where we have used $\int_0^\infty \mathrm{d}\mu \, \cos\mu x = \pi\,\delta(x)$, and the last line by noting that $\delta(\sin\varphi)$ peaks at the ends of the interval where only half peak is sampled, so that both, $\varphi = 0$ and $\varphi = \pi$, contribute $\frac{1}{2}$ each, the latter because $\sin\varphi$ runs backwards there but $\cos\pi = -1$.