Understanding QEq in $BaTiO_3$

Vadim Nemytov

August 31, 2017

Contents

Introduction

0.1 Change in charge on an ion vs. local forces, properties

1) Figure **??** shows how a change in charge on a Ti ion relates to force on that same ion (recall, charges vary only on Ti species). The exact quantity represented by the y-axis is

$$y_{i,I} \equiv \frac{\sqrt{\sum_{\alpha=x,y,z}\left(F^{\alpha}_{i,I}(\{q_l\}) - F^{\alpha}_{i,I}(\bar{q}_{\mathrm{Ba}}, \bar{q}_{\mathrm{Ti}}, \bar{q}_{\mathrm{O}})\right)^2}}{\sum_J \sum_j \sqrt{\sum_{\alpha=x,y,z}\left(F^{\alpha}_{j,J}(\{q_l\})\right)^2}}$$

where $i, j \in \{\mathrm{Ti}_1, ..., \mathrm{Ti}_{27}\}$ and $I, J \in \{\mathrm{MD}_1, ..., \mathrm{MD}_{10}\}$.

2) Figure **??** shows how a large change in charge on a Ti ion relates to forces on that same ion's 6 Oxygen nearest neighbours. The exact quantity represented by the y-axis is:

$$y_{i,I} \equiv \frac{(1/6)\sum_{s\in \mathrm{NN}_i}\sqrt{\sum_{\alpha=x,y,z}\left(F^{\alpha}_{s,I}(\{q_l\}) - F^{\alpha}_{s,I}(\bar{q}_{\mathrm{Ba}}, \bar{q}_{\mathrm{Ti}}, \bar{q}_{\mathrm{O}})\right)^2}}{\sum_J \sum_j \sqrt{\sum_{\alpha=x,y,z}\left(F^{\alpha}_{j,J}(\{q_l\})\right)^2}}$$

where 6 stands for the number of Ti nearest neighbours, $s \in \mathrm{NN}_i = \{s = 1, ..., 6 : \mathrm{R}_{is}$ is nearest neighbour$\}$, $i \in \{\mathrm{Ti}_1, ..., \mathrm{Ti}_{27}\}$, $j \in \{\mathrm{O}_1, ..., \mathrm{O}_{81}\}$ and, as before, $I, J \in \{\mathrm{MD}_1, ..., \mathrm{MD}_{10}\}$. y-axis measures forces on Oxygen ions surrounding a given Ti ion.

3) Figure **??** then examines whether the change in charge on a Ti ion takes place in response to the change in its nearest neighbour structure; namely it looks at the average distance to its neighbours as a measure of how small or large the Oxygen shell around a Ti ions is. The exact value represented by the y-axis is

$$y_{i,I} \equiv \underbrace{(1/6)\sum_{s\in \mathrm{NN}_i}\sqrt{\sum_{\alpha=x,y,z}\left(R^{\alpha}_{s,I} - R^{\alpha}_{i,I}\right)^2}}_{\equiv \bar{\mathrm{R}}^{\mathrm{NN}}_{i,I}} \tag{1}$$

which is simply the average distance to the nearest neighbours of Ti ion i.

4) Figure **??** compares the change in charge to the standard deviation of the distance to nearest neighbour Oxygen ions as compared to the average distance to the shell for a given Ti ion. Defining the expression in equation **??** as $\bar{\mathrm{R}}^{\mathrm{NN}}_{i,I}$, the exact expression represented by the y-axis is:

$$R^{\mathrm{NN}}_{s,i;I} \equiv \sqrt{\sum_{\alpha=x,y,z}\left(R^{\alpha}_{s,I} - R^{\alpha}_{i,I}\right)^2}$$

$$y_{i,I} \equiv \sqrt{\frac{\sum_{s\in \mathrm{NN}_i}\left(R^{\mathrm{NN}}_{s,i;I} - \bar{\mathrm{R}}^{\mathrm{NN}}_{i,I}\right)^2}{6-1}}$$

which stands for the standard deviation of the nearest neighbour bond length from the average.

5) Figure **??** now examines teh relation between the change in charge on a Ti ion and its own dipole moment. The exact quantity represented by the y-axis is defined as:

$$y_{i,I} \equiv \sqrt{\sum_{\alpha=x,y,z} \left(p^{\alpha}_{i,I}(\{q_l\}) - p^{\alpha}_{i,I}(\bar{q}_{\mathrm{Ba}}, \bar{q}_{\mathrm{Ti}}, \bar{q}_{\mathrm{O}}) \right)^2}$$

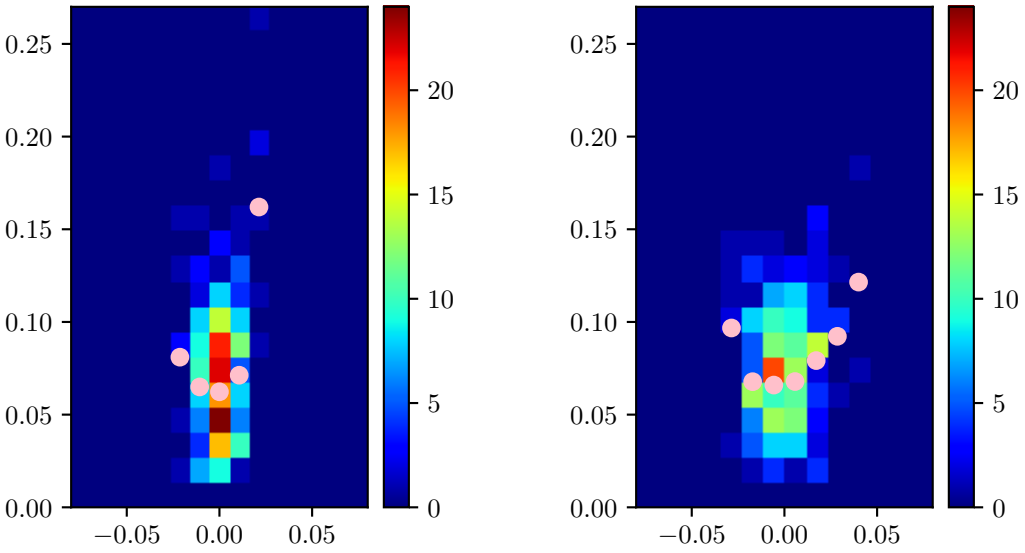
where $i \in \{\mathrm{Ti}_1, ..., \mathrm{Ti}_{27}\}$ and $I \in \{\mathrm{MD}_1, ..., \mathrm{MD}_{10}\}$; the normalization was not performed because dipoles vary by at least two orders of magnitude on different ions[1].

6) Figure **??** looks at the relation between the change in charge on a Ti ion and the dipole moments of its nearest neighbour Oxygen shell. The exact quantity represented by the y-axis is defined as:

$$y_{i,I} \equiv (1/6) \sum_{s \in \mathrm{NN}_i} \sqrt{\sum_{\alpha=x,y,z} \left(p^{\alpha}_{s,I}(\{q_l\}) - p^{\alpha}_{s,I}(\bar{q}_{\mathrm{Ba}}, \bar{q}_{\mathrm{Ti}}, \bar{q}_{\mathrm{O}}) \right)^2}$$

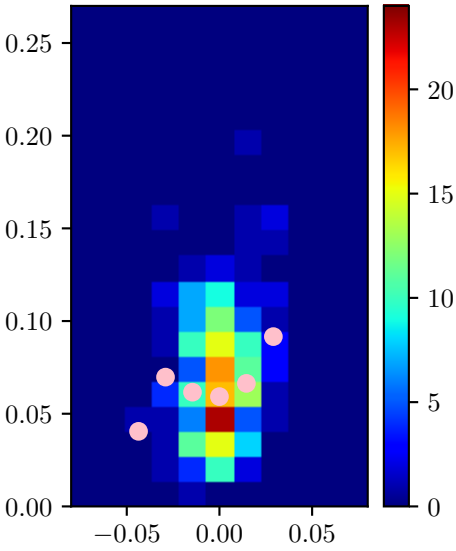
where $i \in \{\mathrm{Ti}_1, ..., \mathrm{Ti}_{27}\}$, $I \in \{\mathrm{MD}_1, ..., \mathrm{MD}_{10}\}$, $s \in \mathrm{NN}_i = \{s = 1, ..., 6 : \mathrm{R}_{is} \text{ is n. n.}\}$ and the normalization was not performed for the reasons mentioned earlier.

[1] Normalizing, as a consequence, leads to a wide amplification of the y-axis.

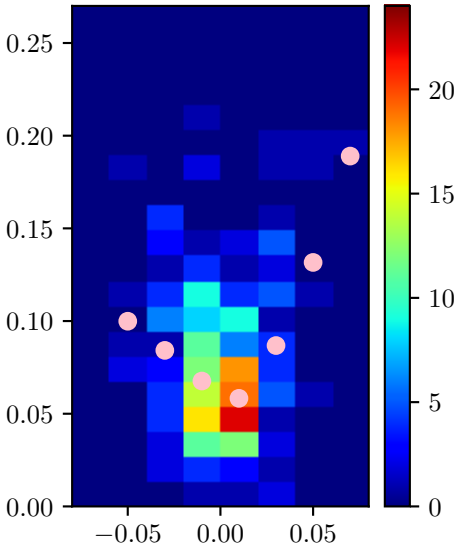


(a) 100 K. Bin size 0.0105e

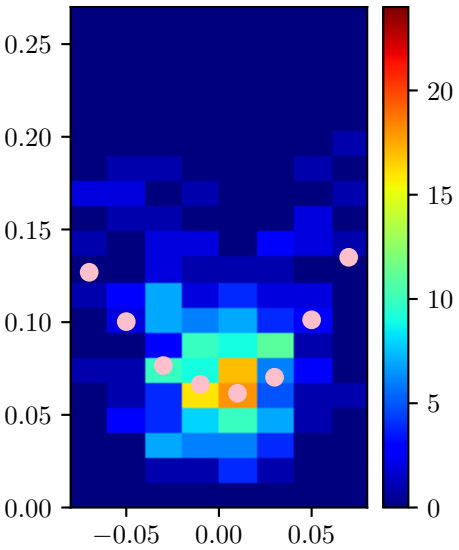
(b) 200 K. Bin size 0.011e



(c) 300 K. Bin size 0.014e

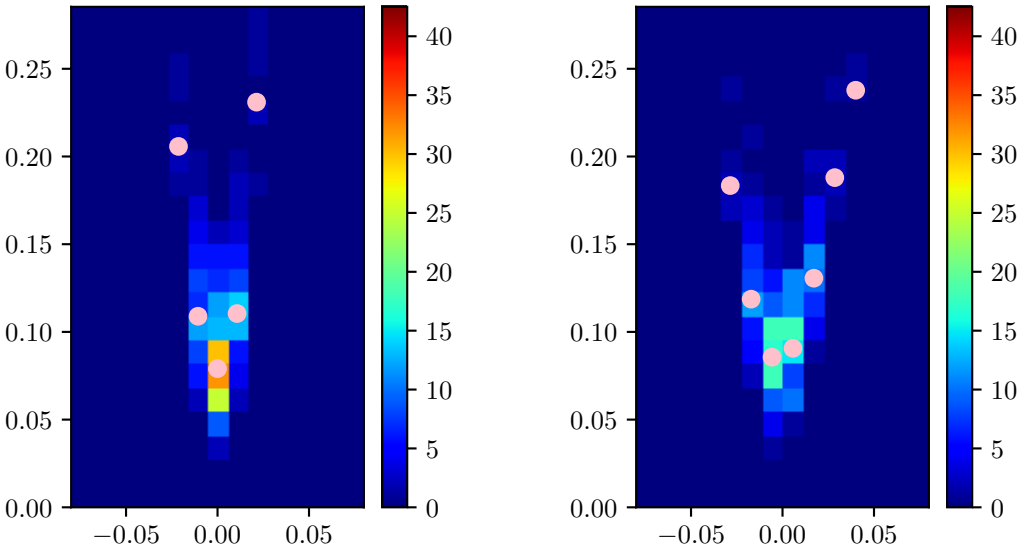


(d) 500 K. Bin size 0.018e



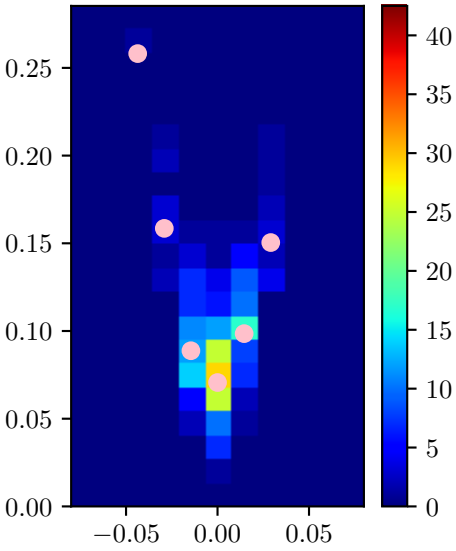
(e) 1000 K. Bin size 0.020e

Figure 1: On-site force on ion, vs its change in charge

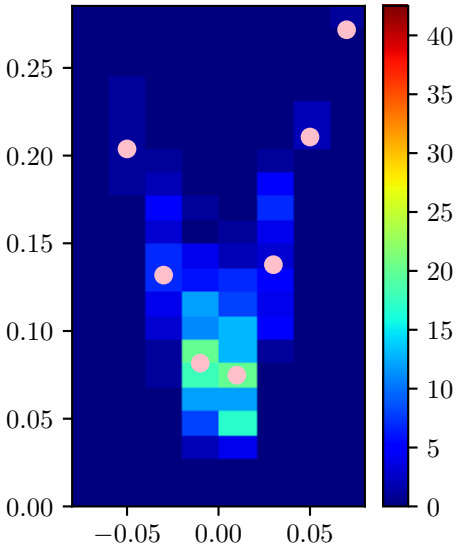


(a) 100 K. Bin size 0.0105e

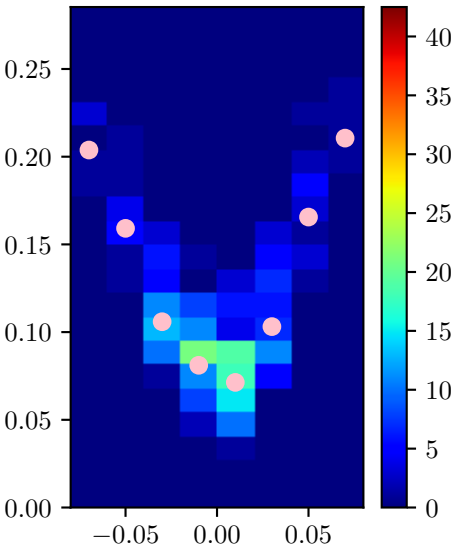
(b) 200 K. Bin size 0.011e



(c) 300 K. Bin size 0.014e

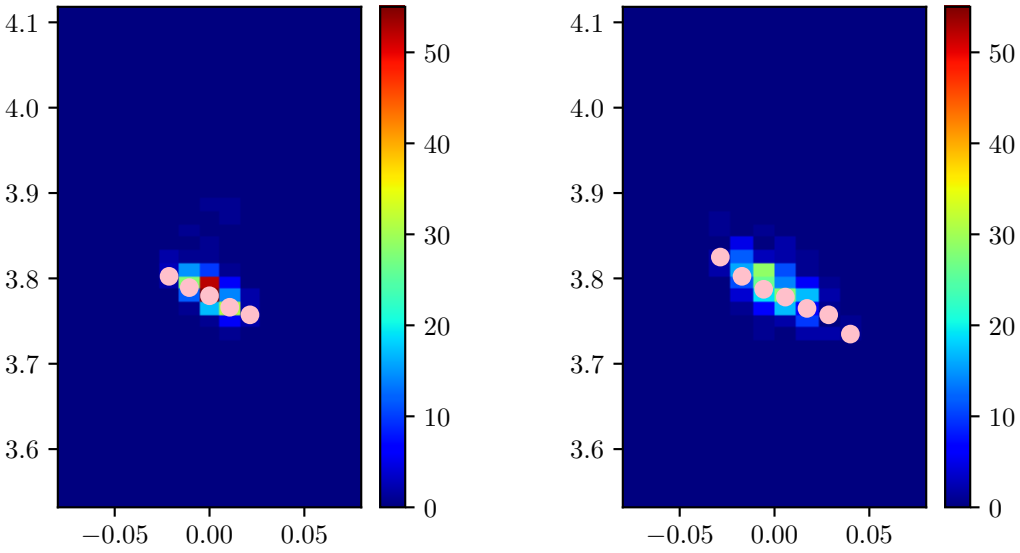


(d) 500 K. Bin size 0.018e



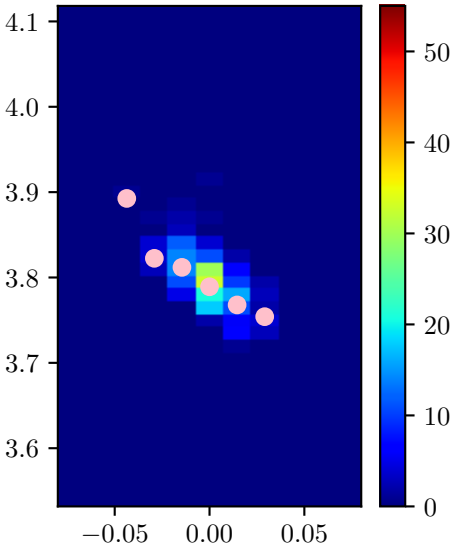
(e) 1000 K. Bin size 0.020e

Figure 2: Forces on nearest neighbours of Ti (Oxygens) vs change in Ti charge

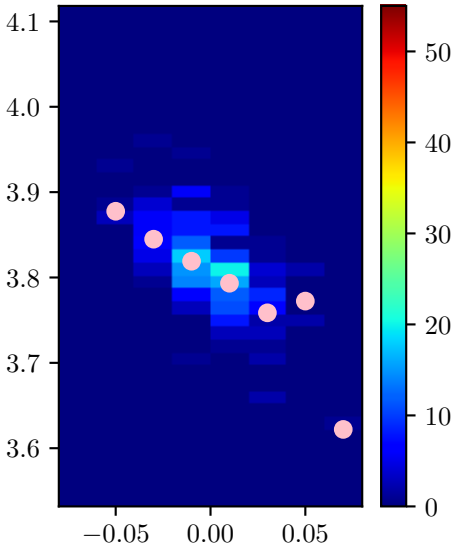


(a) 100 K. Bin size 0.0105e

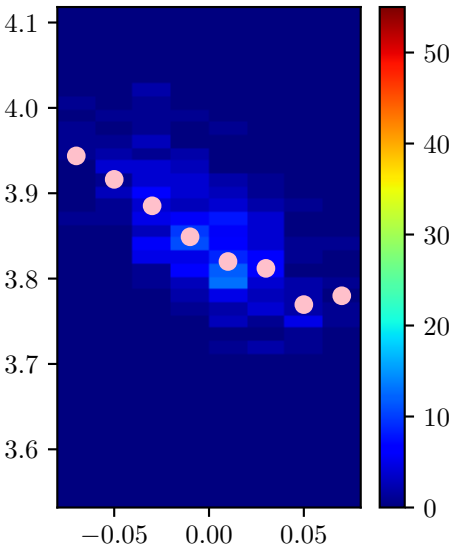
(b) 200 K. Bin size 0.011e



(c) 300 K. Bin size 0.014e

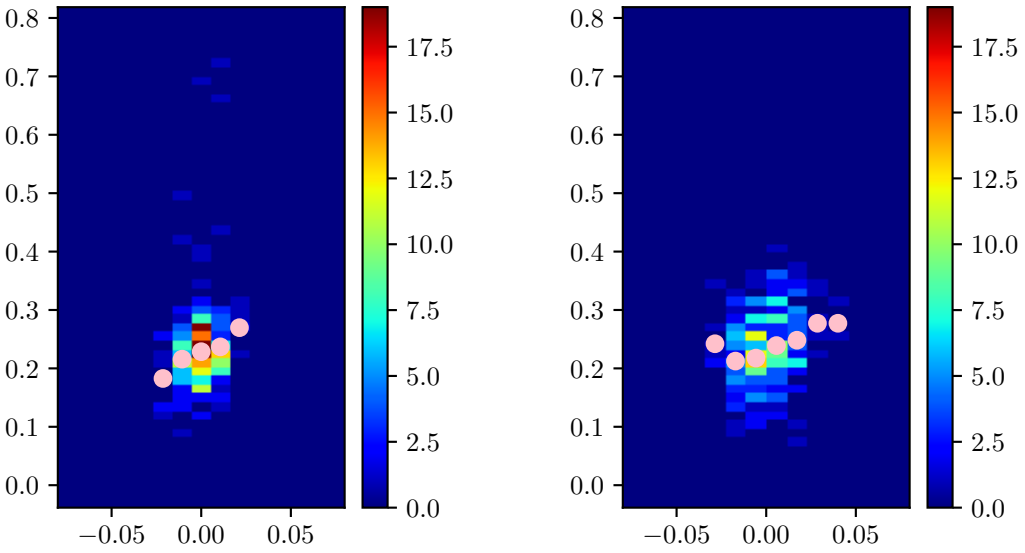


(d) 500 K. Bin size 0.018e



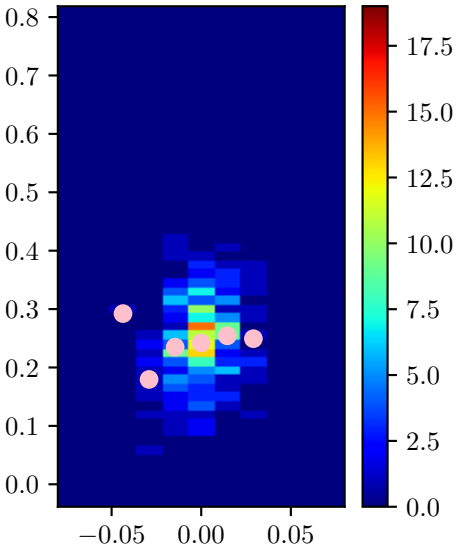
(e) 1000 K. Bin size 0.020e

Figure 3: Change in distance to nearest neighbours of Ti vs change in Ti charge

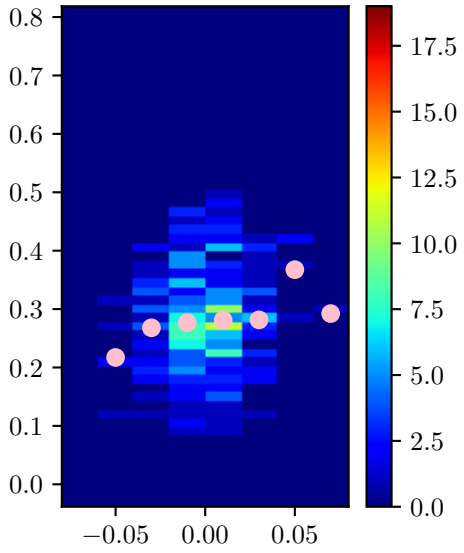


(a) 100 K. Bin size 0.0105e

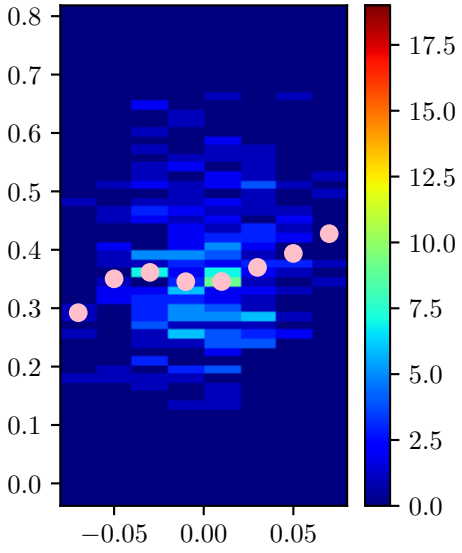
(b) 200 K. Bin size 0.011e



(c) 300 K. Bin size 0.014e

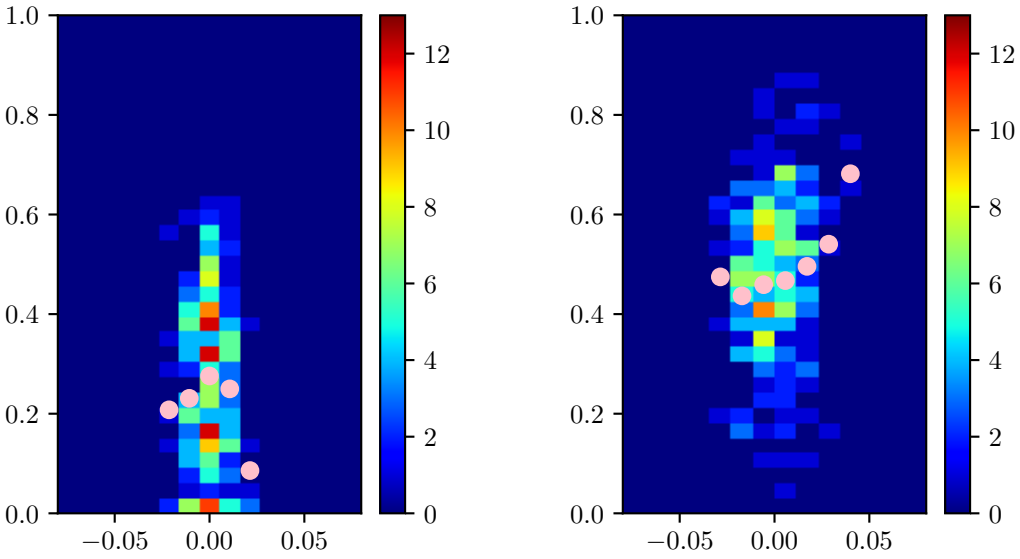


(d) 500 K. Bin size 0.018e



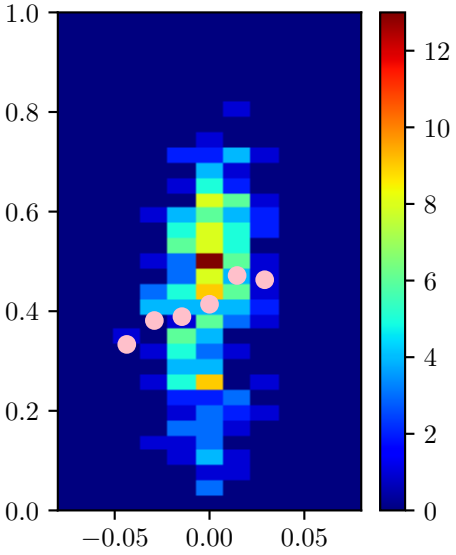
(e) 1000 K. Bin size 0.020e

Figure 4: Change in St.Dev of distance to nearest neighbours of Ti vs change in Ti charge

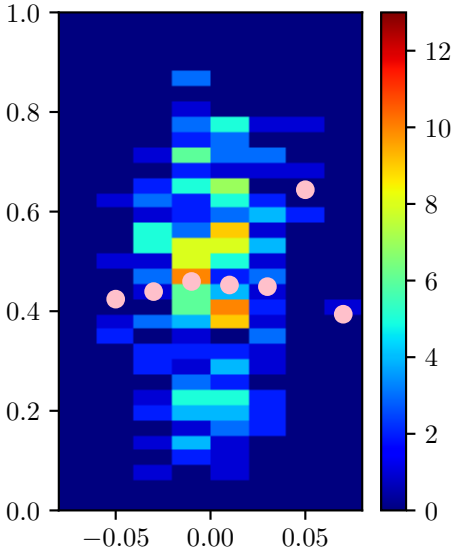


(a) 100 K. Bin size 0.0105e

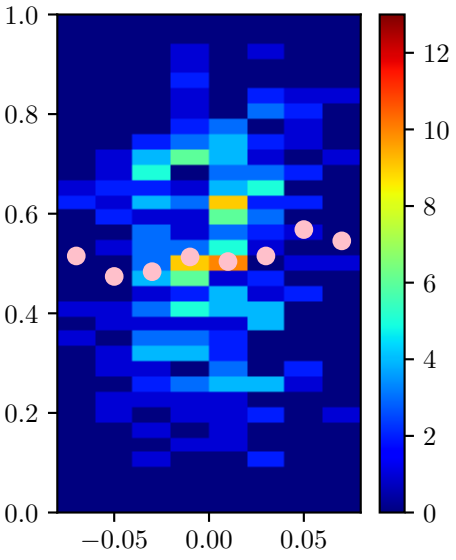
(b) 200 K. Bin size 0.011e



(c) 300 K. Bin size 0.014e

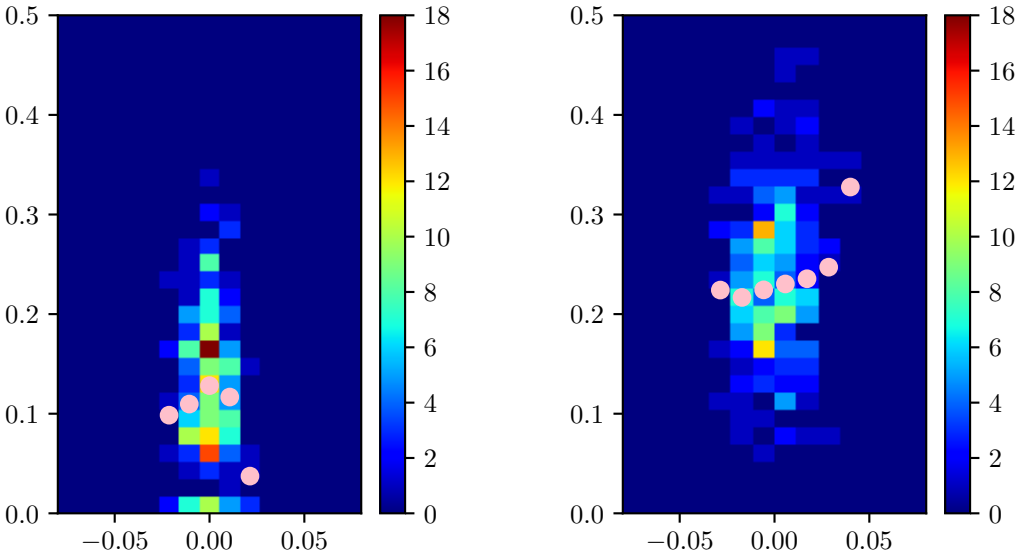


(d) 500 K. Bin size 0.018e



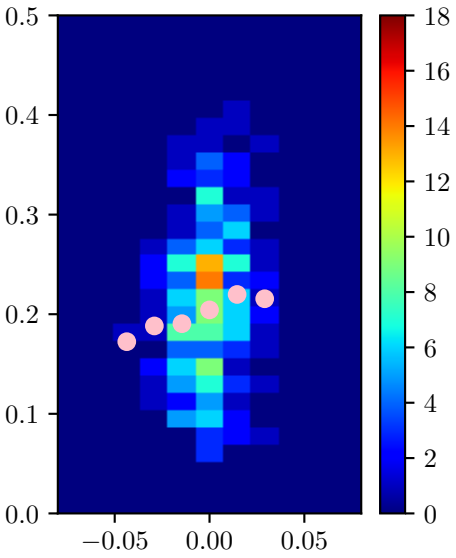
(e) 1000 K. Bin size 0.020e

Figure 5: Change in dipole on an ion vs its change in charge

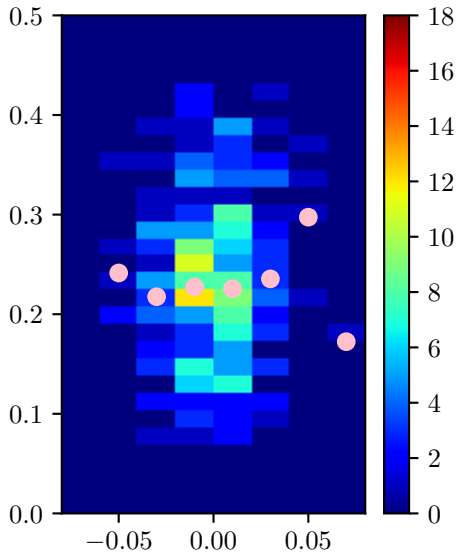


(a) 100 K. Bin size 0.0105e

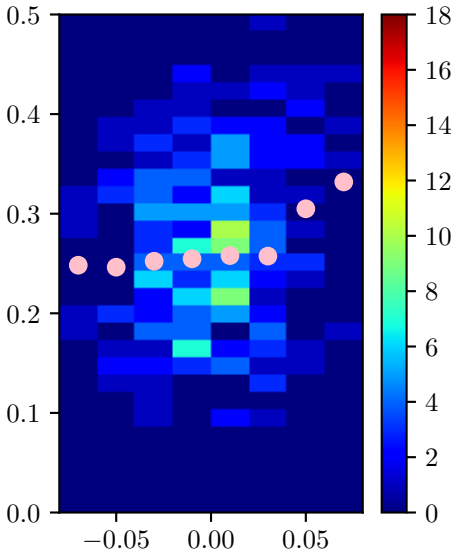
(b) 200 K. Bin size 0.011e



(c) 300 K. Bin size 0.014e



(d) 500 K. Bin size 0.018e



(e) 1000 K. Bin size 0.020e

Figure 6: Change in nearest neighbours' dipoles of Ti vs change in Ti charge