A Molecular Dynamics Simulation of the Orientationally Disordered Phase of Potassium Perchlorate

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Abstract. — The orientationally disordered phase of a relatively large system of potassium perchlorate is simulated on a massively parallel computer with strict SIMD architecture. Crystallographic results are compared with known diffraction data. Correlation densities of orientational and translational variables are computed showing orientation-translation coupling of the perchlorate ions, and coupling between a perchlorate orientation and the translation of neighbouring potassium and perchlorate ions. The orientation-orientation correlation between neighbouring perchlorate ions shows antiferromagnetic pseudo-spin type coupling corresponding to ions in opposite T_d orientations. This correlation has a lifetime which is longer than the single molecule orientational lifetime, evidence of correlated orientational motion.

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1. Introduction

Potassium perchlorate KClO_4 exhibits at approximately $T = 310^\circ\text{C}$ a transition from an orthorhombic [1] (D_{2h}^{16} - Pnma) phase to a fcc [2] (O_h^5 - Fm3m) structure in which the perchlorate ions are orientationally disordered. Neutron diffraction experiments [3] performed on a single crystal of the high temperature phase at 325°C and 420°C , showed that the ClO_4^- ions have preferred orientations of T_d symmetry with orientational disorder (Fig. 1). Such plastic crystals are highly disordered but retain the long range order of the molecular centers of mass thus allowing experiments such as diffraction that would otherwise be impossible. However these experiments are often difficult to interpret, the relevant information being partially smeared out by disorder. A Molecular Dynamics computer simulation (MD) [4], on the other hand, yields extensive information on the simulated system, enabling comparisons with experimental results and precise descriptions.

The present paper presents a simulation of potassium perchlorate in the disordered phase, similar to that in reference [5]. However, the most computer time and memory consuming part in a simulation is the pair force calculation which limits the number of molecules in the simulation to approximately 1000 in most practical cases, and the simulation duration to approximately 100 picoseconds. In many situations, one may wish larger samples for e.g.

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Fig. 1. — The two orientations of the perchlorate ions with T_d symmetry.

long wavelength or small wavenumber studies, and longer durations for e.g. phase transition studies. The use of efficient programming methods, such as a cutoff radius or a neighbour list for short range interactions, an Ewald sum [6] for long range electrostatic forces or the cell multipole method [7] for clusters, can reduce CPU time to a certain extent. However, in order to increase significantly the size of the system, one has to use more powerful computers, and that often translates into parallelism. Our simulation is therefore done on a SIMD (Single Instruction Multiple Data) massively parallel computer in order to be able to study ultimately phase transition dynamics for which all the computational power available is necessary.

In Section 2, some aspects of SIMD parallelism are discussed in relation to MD simulation, along with the description of our potassium perchlorate simulation. We compare in Section 3 our results with diffraction data [3] which was not available to the authors of reference [5]. In Section 4, following a procedure described in [8], we study the single molecule orientation-translation (TO) correlations for the ClO_4 ions, the TO correlations between a perchlorate and a neighbouring potassium ion, and between the translations of one perchlorate ion and the orientation of another. Finally, in Section 5, orientation-orientation (OO) correlations between two neighbouring perchlorate ions are discussed, from both a static and a dynamical point of view.

2. The Simulation

2.1. PARALLELISM. — There are several different types of parallel computers. For the purpose of MD simulations, transputer arrays, which run in MIMD (Multiple Instructions Multiple Data) mode have been used with success [9], and message-passing software such as PVM (Parallel Virtual Machine) also seems promising. Our molecular dynamics simulation was done on a CM2 Connection Machine, a massively parallel computer, with distributed memory; to our knowledge, such architecture was little used up to now for MD. The 16384 processors of the CM2 run in SIMD [10] mode, in which all the processors in use execute the same instruction at the same time using their local data. The 2^n processors are layed out on a n -

Table I. — *Simulation parameters.*

time step ps	cutoff Å	piston mass amu	Cl-O bond length Å	external pressure atm
5.10^{-3}	8.5	300	1.42	1

dimensional hypercube with implicit periodicity in each direction, each processor thus having n neighbours. As in many parallel computing situations, communications between processors are the main problem. The two main communication mechanisms are NEWS (North, East, West, South) [11] very fast communications between neighbours on the grid of the hypercube, and general communications between non-neighbours, which are approximately four times slower.

The CM-FORTRAN compiler automatically allocates arrays to processors according to how the arrays are used in the program. The bulk of a MD simulation program consists of the calculation of the forces between particle pairs i, j , i.e. $\mathbf{f}(r_{ij})$, where $\mathbf{f}$ is the analytical form of the force between two particles at distance r_{ij} and i and j are neighbours. If the program can be written so that the compiler can make neighbouring particles also to be neighbours on the hypercube, then NEWS communications take place. This implies 1) that the crystal structure remains stable throughout the simulation, and 2) that the number of neighbours is smaller than $2n$, where n is the dimensionality of the hypercube. Usually neither condition is met. Because of long-range electrostatic forces, the number of neighbours which must be included in the force calculation can be large, despite the use of Ewald summations. Our simulations are done with a constant number of particles, a constant pressure and a constant enthalpy, i.e. in the NPH ensemble [12], thus allowing the global shape of the system to change when reaching equilibrium, and we wish eventually to be able to simulate phase transitions, for which, clearly the number of neighbours is apt to change. The computer thus follows the non-optimum general communication scheme. Nevertheless, using, to compute forces, neighbours lists defined by a cutoff radius, we were able to simulate large systems ($8 \times 8 \times 8$ cells, a total of 2048 KClO_4 units i.e. 24 576 force centers), in reasonable times: ~ 7.5 s per step for 64 neighbours in the neighbour list, ~ 4 s for 32 neighbours, with neighbour list reactualization every tenth step, despite the time-consuming long range electrostatic forces. Therefore, the sheer power of the 2^n processors compensates for the non-optimum communication situation.

2.2. THE SIMULATION OF POTASSIUM PERCHLORATE. — The main parameters of the simulation (NPH ensemble with periodic boundary conditions, the perchlorate ions being considered rigid) are summarized in Table I. To forbid the rotation of the cell as a whole and to simplify the analysis of the molecular orientations and the crystal structure, the antisymmetric part of the matrix that describes the shape of the cell (matrix $\mathbf{H}$ in [12]) is forced to zero at each step. The main parameters of the simulation are summarized in Table I.

Our initial configuration is a perfect fcc structure for the positions, a temperature adapted Gaussian distribution for translational and angular velocities, and a uniform distribution for the quaternions that describe the orientations of the perchlorate ions. Equilibrium is attained in approximately 5 picoseconds. The positions and the quaternions were saved every twenty steps (0.1 ps).

2.2.1. Short Range Interactions. — The atom-atom short range forces were computed within the cutoff radius given in Table I from a classical exp-6 potential:

$$V^{\text{sr}} = \sum_{i,j,\alpha,\beta} \left(A_{\alpha\beta} \exp(-B_{\alpha\beta} r_{ij\alpha\beta}) - \frac{C_{\alpha\beta}}{r_{ij\alpha\beta}^6} \right) \quad (1)$$

Table II. — *Simulation coefficients for short range potential.*

$\alpha - \beta$	$A_{\alpha\beta}$ (kJ mol ⁻¹)	$B_{\alpha\beta}$ (Å ⁻¹)	$C_{\alpha\beta}$ (kJ mol ⁻¹ (Å ⁶))
K-Cl	221545	3.14	3098
K-K	150100	2.97	1464
K-O	223185	3.52	1301
Cl-Cl	327000	3.31	6554
O-O	331850	4.07	1156
O-Cl	329420	3.69	2753

where $r_{ij\alpha\beta}$ is the distance between atom α of molecule i and atom β of molecule j :

$$r_{ij\alpha\beta} = \|\mathbf{r}_{ij\alpha\beta}\| = \|\mathbf{r}_i^\alpha - \mathbf{r}_j^\beta\| \quad (2)$$

The values of the coefficients $A_{\alpha\beta}$, $B_{\alpha\beta}$ and $C_{\alpha\beta}$ (Tab. II) are the same as in [5].

2.2.2. Long Range Interactions. — With periodic boundary conditions, the simulated cell is replicated throughout space to form an infinite lattice. If $\mathbf{n}$ labels replicated cell of edge L , the total long range electrostatic potential is:

$$V^{\text{lr}} = \sum_{\mathbf{n}} \sum_{i,j,\alpha,\beta} \frac{q_\alpha \cdot q_\beta}{\|\mathbf{r}_{ij\alpha\beta} + \mathbf{n}L\|} \quad (3)$$

where a cubic shaped cell is assumed for simplicity, and q_α is the charge localized on the atom α with the distribution: $q_K = +e$, $q_{Cl} = 0$, $q_O = -0.25e$.

The Ewald sum [6, 12] yields :

$$V^{\text{ewald}} = \sum_{i,j,\alpha,\beta} q_\alpha q_\beta \left(\frac{\text{erfc}(\eta r_{ij\alpha\beta})}{r_{ij\alpha\beta}} + \frac{2\pi}{V} \sum_{\mathbf{q} \neq \mathbf{0}} \frac{1}{q^2} \exp\left(-\frac{q^2}{4\eta^2}\right) \cos(\mathbf{q} \cdot \mathbf{r}_{ij\alpha\beta}) - \frac{\eta}{\sqrt{\pi}} \right) \quad (4)$$

where $\text{erfc}(x)$ is the complementary error function, and η a parameter that accelerates the convergence. The sum $\sum_{i,j,\alpha,\beta}$ ranges in principle over all the charges in the cell, but due to the rapid convergence of $\text{erfc}(x)$, the first term is limited to the same cutoff radius as the short range forces and thus can be treated similarly. The long range part of the potential is computed in reciprocal space using the periodicity of the replicated cells.

Potential V^{ewald} gives a very good approximation of V^{lr} with a fast convergence if parameter η is properly chosen. In order to choose the best value for η [13], Figure 2 shows V^{ewald} and $F^{\text{ewald}} = \sum \|\mathbf{f}\|^2$, the sum of squared forces, for different values of η and the cutoff radius. We finally retained $\eta = \frac{16}{L}$, so that the results are fairly independent of both η and of the cutoff radius.

3. Comparison with Diffraction Experiments

The simulations were done at two temperatures in the plastic phase. In both cases, the correct fcc structure was obtained. Figure 3 shows the orientational probability density function $P(\Omega)$, where Ω denotes the orientation of a perchlorate ion i.e. the rotation of Euler angles ψ , θ and ϕ that rotates the molecular reference frame unto the crystal frame. Given that the orientational origin is a T_d orientation in which the four molecular threefold axes are parallel to four of the eight crystal ones ($[\bar{1}\bar{1}1]$, $[\bar{1}1\bar{1}]$, $[1\bar{1}\bar{1}]$, $[\bar{1}\bar{1}\bar{1}]$), Figure 3 shows peaks in the T_d orientations in

Fig. 2. — Ewald sum parameters: a) V^{ewald} and b) $F^{\text{ewald}} = \sum \|\mathbf{f}\|^2$ for cutoff radius of 8.5, 8.0, 7.0 and 6.0 Å as functions of ν where $\eta = \nu/L$, and L is the box size.

Table III. — *Lattice constant.*

T (°C)	Simulation (Å)	Experiment (Å)
325	7.68	7.522 ± 0.002
420	7.75	7.58 ± 0.01

accordance with experimental results. The streaks for $\beta \simeq 0$ and $\beta \simeq 180^\circ$ on Figure 3 are caused by the singularity inherent to Euler angle representation. Table III compares simulation and experimental lattice constants.

In order more precisely to compare the simulation with experiment, an expansion of the molecular orientational probability density function $P(\Omega)$ on a set of rotators functions $R_{\lambda\lambda'}^l(\Omega)$

Fig. 3. — Orientational probability density function of the ClO_4 ions, calculated over a 100 ps run at $T = 325^\circ\text{C}$, as a function of the Euler angles (Ψ, θ, φ) . The streaks for $\theta \sim 0$ (resp. $\theta \sim \pi$) are due to Ψ and φ (resp. Ψ and $-\varphi$) being undistinguishable.

adapted to the symmetries of the ion and of the crystalline site was used [14]:

$$P(\Omega) = \sum_{\ell, \lambda, \lambda'} \frac{2\ell + 1}{8\pi^2} A_{\lambda\lambda'}^\ell R_{\lambda\lambda'}^\ell(\Omega) \quad (5)$$

where $A_{\lambda\lambda'}^\ell$ denotes the coefficients of the expansion. Because of the invariance of $P(\Omega)$ with respect to the symmetry operations of the site group and of the molecular group, only few expansion coefficients $A_{\lambda\lambda'}^\ell$ are non zero [15]. In the case of ClO_4^- the first non zero coefficients are: A_{11}^4 , A_{11}^6 , A_{11}^8 , A_{11}^{10} . The coefficient A_{11}^0 is taken to be equal to 1 due to the normalization condition of $P(\Omega)$. This allows to compute a structure factor that can be fitted to neutron diffraction results. Therefore, the first coefficients of the expansion and the two translational disorder terms, $\langle u^2 \rangle_K$ for potassium and $\langle u^2 \rangle_{\text{ClO}_4}$ for the perchlorate center of mass motion, were computed from:

Table IV. — Comparison of the simulation and experimental results, using an expansion on a set of symmetry adapted functions at two temperatures. The experimental results were obtained by fitting the model to Bragg peak intensities. Bragg peaks were computed from the simulation and the model fitted to them, then the same parameters were computed directly. Had all the perchlorate ions been in perfect T_d orientations, all coefficients $A_{\lambda\lambda'}$ would have been equal to 1

$T = 325\text{ }^\circ\text{C}$	experiment	simulat.(Bragg)	simulat.(direct)
A_{11}^4	0.44 ± 0.03	0.60 ± 0.04	0.21
A_{11}^6	0.07 ± 0.02	-0.07 ± 0.21	0.14
A_{11}^8	0.45 ± 0.17	0.95 ± 1.06	0.054
A_{11}^{10}	0.10 ± 0.18	0.68 ± 0.94	0.03
$\langle u_x^2 \rangle_{K^+}$	0.101 ± 0.006	0.101 ± 0.016	0.095
$\langle u_x^2 \rangle_{\text{ClO}_4^-}$	0.093 ± 0.002	0.119 ± 0.012	0.115

$T = 420\text{ }^\circ\text{C}$	experiment	simulat.(Bragg)	simulat.(direct)
A_{11}^4	0.41 ± 0.03	0.55 ± 0.09	0.16
A_{11}^6	0.05 ± 0.03	0.03 ± 0.40	0.10
A_{11}^8	0.36 ± 0.20	0.42 ± 2.10	0.03
A_{11}^{10}	-0.04 ± 0.24	0.28 ± 1.93	0.02
$\langle u_x^2 \rangle_{K^+}$	0.119 ± 0.007	0.123 ± 0.030	0.12
$\langle u_x^2 \rangle_{\text{ClO}_4^-}$	0.110 ± 0.003	0.131 ± 0.024	0.14

- a) the neutron experiment,
- b) the simulation, by computing same number of Bragg peak intensities as in the experiment, and then feeding them into the same model as if it were a real experiment, and,
- c) the simulation, directly from the molecular positions and orientations.

These three sets of coefficients [16] allow to compare experimental and simulation results. By comparing a) and b) one checks the validity of the simulation, and by b)–c) comparison, the model used by the experimentalists. Table IV summarizes these results. In all cases the translational disorder as given by $\langle u_x^2 \rangle_{K^+}$ and $\langle u_x^2 \rangle_{\text{ClO}_4^-}$ are consistent within a very good approximation.

The situation however is more complex for the orientational disorder. The expansion coefficients obtained from the Bragg peak fitting of the experiments and the simulation (a)–b) comparison), while relatively close at both temperatures at least for the lower values of ℓ , are significantly weaker for the experiment than for the simulation. This means that the simulation is orientationally less disordered than the real sample, since the situation in which all coefficients vanish to zero corresponds to isotropy. On the other hand, the directly computed coefficients are much weaker than the fitted ones (b) vs. c)). The orientations of the maxima of the opdf are unaffected by these variations, therefore the most probable orientations are of T_d symmetry in all cases. However, this analysis shows that while the expansion method yields the correct symmetry, it is unreliable when quantitative results are required, presumably because of the small number of experimental data.

4. Orientation-Translation Correlations at $T = 325^\circ\text{C}$

Since the simulation reproduces reasonably well known crystallographic data, we may proceed to more sophisticated quantities. We wish to estimate the correlations between the set of variables $\{x_1, \dots, x_p\}$ (e.g. molecular center-of-mass positions) and the set $\{x_{p+1}, \dots, x_n\}$ (e.g. molecular orientations). The correlation densities:

$$C(x_1, \dots, x_p; x_{p+1}, \dots, x_n) = P(x_1, \dots, x_p, x_{p+1}, \dots, x_n) - P(x_1, \dots, x_p)P(x_{p+1}, \dots, x_n)$$

where P denotes probability density function of a set of variables $\{x_i\}$, are computed following the methods detailed in reference [8], and summarized in Appendix A.

4.1. SINGLE MOLECULE TO CORRELATIONS

4.1.1. Symmetry. — The single molecule TO correlation density $C(u_r; \eta, \zeta)$ was calculated for the perchlorate ion, u_r being the molecular center of mass displacement projected on a direction $\mathbf{r}$ and (η, ζ) the polar angles that define the orientations of the perchlorate threefold symmetry axes, i.e. the Cl–O bonds. It turns out to be an even function of u_r for all (η, ζ) as apparent in Figure 4 for $\mathbf{r} // [110]$. This ‘experimental’ fact is rather unexpected as the only constraint on $C(u_r; \eta, \zeta)$ is that

$$\int_{-\infty}^{+\infty} C(u_r; \eta, \zeta) du_r = 0 \quad (6)$$

— and the equivalent for (η, ζ) integration — which does not require any given symmetry. Indeed, an odd function of u_r would seem natural, as it would simply displace slightly the maximum of the single molecule TO probability density $P(u_r, \eta, \zeta)$, meaning that for a given orientation (η, ζ) , the molecular center of mass is moved by a certain quantity, resulting in a straightforward TO coupling situation. On the other hand, an even function yields a narrowing or a broadening of $P(u_r, \eta, \zeta)$, depending on whether the central part of the function is positive or negative, with no displacement. This seems reasonable when orientation (η, ζ) corresponds to a high symmetry direction of the crystal but is surprising in general orientation.

Following our results, however, the correlation density was fitted with the two parameter function:

$$C(u_r; \eta, \zeta) = A_{\eta, \zeta} \left(1 - 2 \left(\frac{u_r}{\gamma_{\eta, \zeta}} \right)^2 \right) \exp \left[- \left(\frac{u_r}{\gamma_{\eta, \zeta}} \right)^2 \right] \quad (7)$$

which both is even and has the correct property of equation (6). This is not a model, but only a function with convenient properties. For a direction (η, ζ) , $A_{\eta, \zeta}$ represents the magnitude of the correlations and $\gamma_{\eta, \zeta}$ is directly proportional to the molecular translational motion. When for a given orientation (η, ζ) , $A_{\eta, \zeta} > 0$, it means that $C_{\eta, \zeta} > 0$ for $-\frac{\gamma_{\eta, \zeta}}{\sqrt{2}} < u_r < +\frac{\gamma_{\eta, \zeta}}{\sqrt{2}}$, that is, the molecular centers of mass tend to stay closer to their mean positions than if there were no TO correlation. Conversely, $A_{\eta, \zeta} < 0$ yields two maxima at $\pm \sqrt{\frac{3}{2}} \gamma_{\eta, \zeta}$ resulting in a broadening of the translational distribution due to TO coupling.

4.1.2. $\mathbf{r} // [110]$. — In the following, the pixel size is $15^\circ \times 15^\circ$ in the (η, ζ) plane. We now discuss the results for the projection direction $\mathbf{r} // [110]$, the first neighbour direction in the fcc lattice.

The fit of expression (7) to $C(u_r; \eta, \zeta)$, yields $A_{\eta, \zeta}$, shown on Figure 5 as a function of η and ζ . The eight maxima are for the molecular threefold axes parallel to the crystal threefold axes ($\eta \sim 55^\circ$, $\zeta = 45^\circ$; .), i.e. for T_d molecular orientations. Therefore, for these orientations, the center of mass translational displacements along the $[110]$ direction tend to be smaller than suggested

Fig. 4. — Single molecule TO correlation, $C(u; \eta, \zeta)$ with center of mass displacement $\mathbf{u}$ projected on the $[110]$ direction.

by the value of $\langle u_r^2 \rangle_{\text{ClO}_4}$. Indeed the halfwidth of the central peak is $\frac{\gamma_{\eta, \zeta}}{\sqrt{6}} \simeq 0.2 \text{ \AA}$, when the parameter $A_{\eta, \zeta}$ is not too small, which is smaller than the translational disorder $\sqrt{\langle u_r^2 \rangle_{\text{ClO}_4}} \sim 0.3 \text{ \AA}$ (cf Tab. 4). Elsewhere, in non T_d orientations ($\eta = 90^\circ, \zeta = 90^\circ$), where $A_{\eta, \zeta} < 0$, the molecular centers of mass tend to undergo larger displacements of approximately $0.6 \text{ \AA}$. We obtain therefore a narrowing of translational disorder in the most probable orientations of T_d symmetry, and a broadening due to TO coupling in non T_d orientations. The ClO_4 ions are thus submitted to TO coupling that displaces them away from their mean center of mass position when in process of reorienting, the displacement distribution being symmetric with respect to the crystal site.

These results are quite different from those obtained using the same method in neopentane [8] for which TO coupling also takes place when the molecules are not in their most probable

Fig. 6. — Correlation density between the orientation of a perchlorate ion and the translation of a potassium ion: $C(u_{r_1}; \eta_2, \zeta_2)$. The connecting vector is: $\mathbf{s}_{1,2} = [\frac{1}{2}, 0, 0]$.

from the [100] direction. The attractive electrostatic forces between the ions K^+ and ClO_4^- ($q_{\text{O}} = -0.25e, q_{\text{K}} = +e$) are completely negligible because, at this distance, it is the short range steric hindrance that is dominant. Conversely when the potassium ion moves away on the [100] direction, the T_d orientation of the first neighbour perchlorate is not favored.

4.2.2. Perchlorate-Perchlorate Coupling. — The analysis is the same as for potassium-perchlorate coupling but Figure 8 shows that $(\text{K}^+ - \text{ClO}_4^-)$ correlations are much stronger than $(\text{ClO}_4^- - \text{ClO}_4^-)$ correlations, which can be explained by the shorter distance.

5. Orientation-Orientation Correlations

Clearly, for OO correlations, both molecules 1 and 2 are perchlorate ions and $\mathbf{s}_{1,2} = [\frac{1}{2}, \frac{1}{2}, 0]$. Figure 9 shows the orientation-orientation correlation density $C(\alpha_1; \alpha_2, \beta_{1,2})$ where α_1 (resp. α_2) is the angle between the Cl—O bond of molecule 1 (resp. 2) and the connecting vector

Fig. 7. — Amplitude of the correlation density between the orientation of a perchlorate ion and the translation of a potassium ion $A_{\eta, \zeta}$, using equation (8). The projection direction is $[100]$. The connecting vector is $\mathbf{s}_{1,2} = [\frac{1}{2}, 0, 0]$.

Fig. 8. — Angular dependence of the two molecule TO correlation amplitude $A_{\eta, \zeta}$ using equation (8), where the projection direction is $[110]$. The connecting vector is $\mathbf{s}_{1,2} = [\frac{1}{2}, \frac{1}{2}, 0]$.

$\mathbf{s}_{1,2}$, and $\beta_{1,2}$ is the dihedral angle between the planes that contain $\mathbf{s}_{1,2}$ on the one hand, and the Cl—O bonds of molecules 1 and 2 on the other [8]. The maxima visible on Figure 9 are compatible with the two molecules being in two opposite T_d orientations, e.g. the bond of molecule 1 are in $[111]$, $[\bar{1}\bar{1}\bar{1}]$, $[1\bar{1}\bar{1}]$ and $[\bar{1}\bar{1}1]$ while those of molecule 2 are in directions $[\bar{1}\bar{1}1]$, $[\bar{1}\bar{1}\bar{1}]$, $[11\bar{1}]$ and $[\bar{1}\bar{1}\bar{1}]$ (Fig. 10). The minima on Figure 9 on the other hand are compatible with the two molecules being in the same T_d orientation. This is similar to an antiferromagnetic coupling of spins.

Fig. 9. — OO correlation density $C(\alpha_1; \alpha_2, \beta_{1,2})$, of two neighbouring perchlorate ions. The connecting vector is $\mathbf{s}_{1,2} = [\frac{1}{2}, \frac{1}{2}, 0]$.

5.1. PSEUDOSPIN MODEL. — Thus, if x, y , and z are the coordinates of the oxygen atoms in a reference frame whose axes are parallel to those of the crystal frame, but centered on the Cl atom of that ion, we define for each molecule a pseudospin σ such that:

- if $(x > 0, y > 0, z > 0)$, $(x < 0, y < 0, z > 0)$, $(x < 0, y > 0, z < 0)$ and $(x > 0, y < 0, z < 0)$, we assume that this molecule is in one of the T_d orientations and write $\sigma = 1$.
- if $(x > 0, y > 0, z < 0)$, $(x < 0, y < 0, z < 0)$, $(x < 0, y > 0, z > 0)$ and $(x > 0, y < 0, z > 0)$, the molecule is in the other T_d orientations and write $\sigma = -1$.
- and if neither condition is verified, we assume that this molecule is in non- T_d orientation and write $\sigma = 0$.

Table V shows $P(\sigma)$ at both temperatures. In an Arrhenius model, this yields an activation energy of approximately 530 K for the higher energy non- T_d state, a relatively low value [17].

Fig. 10. — Two perchlorate ions in different T_d orientations, an occurrence which corresponds to the maxima of the OO correlation density $C(\alpha_1; \alpha_2, \beta_{1,2})$. This leads to the hypothesis of pseudospins with antiferromagnetic type coupling.

Table V. — $P(\sigma)$ for both simulation temperatures, where σ is the pseudospin associated with T_d orientations. T_0 is given by: $P(\sigma = 0) = e^{\frac{-T_0}{T}}$.

T (°C)	σ		
	-1	0	1
325	0.29	0.42	0.29
420	0.27	0.46	0.27

With this definition, the OO correlation can be written as a pseudospin-pseudospin correlation density:

$$C(\sigma_1; \sigma_2) = P(\sigma_1, \sigma_2) - P(\sigma_1)P(\sigma_2) \quad (9)$$

Table VI gives $C(\sigma_1; \sigma_2)$ for which $C(-1; -1) = C(+1; +1) = -C(-1; +1) = -C(+1; -1)$ corresponds to the antiferromagnetic coupling inferred from Figure 9. Another way to see this is to calculate the usual correlation function:

$$\langle \sigma_1 \sigma_2 \rangle = \sum_{\sigma_1, \sigma_2} C(\sigma_1; \sigma_2) \sigma_1 \sigma_2 \quad (10)$$

given that $\langle \sigma_1 \rangle = \langle \sigma_2 \rangle = 0$. Using the results given in Table VI, this yields $\langle \sigma_1 \sigma_2 \rangle = -0.0185$ at $T = 325$ °C and -0.0108 at $T = 420$ °C, at the same time clearly negative and strongly temperature dependent.

The terms in Table VI that correspond to $\sigma = 0$, i.e. the middle line and column, show that there is very little, if any, correlation of $\sigma = 0$ spins with $\sigma = \pm 1$ spins. Now, an antiferromagnetic structure on a fcc lattice should generate frustration, which the possibility for $\sigma = 0$ however prevents in our case. An ordered, frustration-free structure could be constituted of a succession of planes with $\sigma = \pm 1$ and planes with $\sigma = 0$, thus $P(\sigma = 0) = 0.5$, $P(\sigma = 1) = P(\sigma = -1) = 0.25$, and $\langle \sigma_1 \sigma_2 \rangle = -\frac{1}{6}$. While the probabilities are comparable to ours, the value taken by the correlation function is an order of magnitude greater. The situation in our simulation is thus that of a highly disordered system with a weak antiferromagnetic coupling.

Table VI. — Correlation density of neighbouring pseudospins $C(\sigma_1; \sigma_2) \times 10^4$.

$T = 325\text{ }^\circ\text{C}$				$T = 420\text{ }^\circ\text{C}$			
σ	-1	0	1	σ	-1	0	1
-1	-43	-4	47	-1	-24	-2	26
0	-7	9	-2	0	-6	4	2
1	50	-5	-45	1	30	-2	-28

Table VII. — Perchlorate reorientation time calculated from the average kinetic energy (first line) where $\Delta\eta = \pi/2$, and I is the moment of inertia, pseudospin residence time where: $\langle\sigma_1(0)\sigma_1(t)\rangle = \langle\sigma_1(0)\sigma_1(0)\rangle \exp(-t/\tau_{11})$ (second line), and pseudospin correlation time where: $\langle\sigma_1(0)\sigma_2(t)\rangle = \langle\sigma_1(0)\sigma_2(0)\rangle \exp(-t/\tau_{12})$ (third line), all given in picoseconds.

T	325 °C	420 °C
$\tau_0 = \Delta\eta\sqrt{\frac{I}{k_b T}}$	0.65	0.60
τ_{11}	0.45	0.30
τ_{12}	0.65	0.55

5.2. CORRELATED ORIENTATIONAL DYNAMICS.. — Using the pseudospin model, the orientational dynamics are easy to describe. Table VII gives some characteristic orientational times all of which are of the order of 0.5 ps. The first, τ_0 , is the time necessary to do a 90° rotation, that is, the time it takes to go from a $\sigma = 1$ to a $\sigma = -1$ state, or *vice versa*, with the average angular velocity due to temperature. The quantity $\langle\sigma_1(0)\sigma_1(t)\rangle$ can be computed as a function of time, and fitted with: $\langle\sigma_1(0)\sigma_1(0)\rangle \exp(-t/\tau_{11})$ (Fig. 11). Thus, τ_{11} is the residence time

Fig. 11. — Orientational dynamics of the pseudospins at $T = 325\text{ }^\circ\text{C}$. $\langle\sigma_1(0)\sigma_1(t)\rangle$ (line) fitted with $\langle\sigma_1(0)\sigma_1(0)\rangle e^{(-t/\tau_{11})}$ (open squares), and $\langle\sigma_1(0)\sigma_2(t)\rangle \times 10$ (line) fitted with $\langle\sigma_1(0)\sigma_2(0)\rangle e^{(-t/\tau_{12})}$ (crosses).

of a spin in one of its ± 1 states. τ_0 is approximately the residence time in state $\sigma = 0$, confirmed by the fact that $\tau_0/\tau_{11} \sim P(\sigma = 0)/P(\sigma = 1)$ as given in Table V. In a similar fashion, $\langle \sigma_1(0)\sigma_2(t) \rangle$, yields τ_{12} , the time during which two neighbouring spins remain opposed. The noteworthy result is that $\tau_{12} > \tau_{11}$, which shows that molecular reorientations have, to some extent, a collective character, despite the weak coupling mentioned above. It appears that since the focus up to now in plastic crystal studies was on *individual* orientational motion (see e.g. the review paper [18]), it is the first time correlated orientational motion is observed. It would have been extremely difficult to show, had not the pseudospin model been valid. It is worth stressing, at this point, that this model was not chosen *a priori*, but arises naturally from our data.

6. Summary and Conclusion

The disordered phase of potassium perchlorate was simulated on a massively parallel computer with strict SIMD architecture. While it is difficult, for such applications, to use that architecture optimally, a large sample was simulated in a reasonable time.

The results are consistent with diffraction experiments, regarding lattice constant, translational disorder, and the symmetry of the most probable orientations of the perchlorate ions. The expansion of the molecular orientational probability density function that had been used to interpret the experiments was thoroughly tested and proved reliable for the translational disorder contribution but only for the main features of the orientational probability density function.

The orientation-translation correlations of the perchlorate ions show that when a molecule is in one of its two T_d most probable orientations, its center-of-mass motion is reduced with respect to mean translational disorder, while non- T_d oriented molecules tend to show larger displacements. The TO correlation between the orientation of a ClO_4 molecule and the translation of a neighbouring perchlorate ion shows preference for molecular T_d orientations when the neighbouring ion moves closer to the molecule. The correlation between the orientation of a perchlorate ion and the translation of a potassium ion shows a similar but weaker effect.

Finally, the orientational correlations between two neighbouring perchlorate molecules display a pseudospin type antiferromagnetic coupling. The study of the dynamics of these spins show that two neighbouring ions tend to remain orientationally coupled longer than the individual residence time in one of the $\sigma = \pm 1$ states. This is the first, to our knowledge, evidence of collective orientational motion in such crystals.

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Appendix A

Correlation Densities

We describe here, as an example, the computation of the correlation density $C(\mathbf{u}; \Omega)$ where $\mathbf{u}$ is the molecular center-of-mass displacement with respect to the mean molecular position, and Ω is a set of Euler angles that yield the molecular orientation with respect to a crystal reference frame. This is a six-variable function which can be replaced by a much more convenient three-variable function:

$$C(u_r; \eta, \zeta) = P(u_r, \eta, \zeta) - P(u_r)P(\eta, \zeta) \quad (\text{A.1})$$

where $u_r = \mathbf{u} \cdot \mathbf{r}$ is the projection of $\mathbf{u}$ on a given direction $\mathbf{r}$, and (η, ζ) are the polar angles of a Cl–O bond in the perchlorate ion.

The simulation yields the orientational probability density $P(\eta, \zeta)$ as a sum of Dirac δ -functions:

$$P(\eta, \zeta) = \frac{1}{N} \sum_{i=1}^N \frac{\delta(\eta - \eta_i)}{\sin \eta_i} \delta(\zeta - \zeta_i) \quad (\text{A.2})$$

where N is the product of the number of bonds in one ion by the number of ions and the number of timesteps in the simulation. (η_i, ζ_i) are the polar angles of bond i .

We must however use pixels of finite size, and thus define a coarse-grained probability density:

$$\begin{aligned} \bar{P}(\eta, \zeta) &= \frac{\int_{\eta}^{\eta+\Delta\eta} \int_{\zeta}^{\zeta+\Delta\zeta} P(\eta, \zeta) \sin \eta \, d\eta \, d\zeta}{\int_{\eta}^{\eta+\Delta\eta} \int_{\zeta}^{\zeta+\Delta\zeta} \sin \eta \, d\eta \, d\zeta} \\ &= \frac{\nu_o(\eta, \zeta)}{(\cos \eta - \cos(\eta + \Delta\eta)) \Delta\zeta} \end{aligned} \quad (\text{A.3})$$

where $\nu_o(\eta, \zeta)$ is the fraction of bonds for which $\eta \leq \eta_i < \eta + \Delta\eta$, $\zeta \leq \zeta_i < \zeta + \Delta\zeta$. Treating $P(u_r)$ and $P(u_r, \eta, \zeta)$ in a similar fashion, the coarse-grained correlation density writes:

$$\bar{C}(u_r; \eta, \zeta) = \frac{\nu_{to}(u_r, \eta, \zeta) - \nu_t(u_r)\nu_o(\eta, \zeta)}{(\cos \eta - \cos(\eta + \Delta\eta)) \Delta\zeta} \quad (\text{A.4})$$

with obvious notations, the subscript o standing for *orientational* and t for *translational*.

This method can be extended in a straightforward manner to other correlation densities.

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