Test of a simple and flexible molecule model for $\alpha$-, $\beta$- and $\gamma$-S$_8$ crystals

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S$_8$ is the most stable compound of elemental sulfur in solid and liquid phases, at ambient pressure and below 400K. Three crystalline phases of S$_8$ have been clearly identified in this range of thermodynamic parameters, although no calculation of its phase diagram has been performed yet. $\alpha$- and $\gamma$-S$_8$ are orientationally ordered crystals while $\beta$-S$_8$ is measured as orientationally disordered. In this paper we analyze the phase diagram of S$_8$ crystals, as given by a simple and flexible molecule model, via a series of molecular dynamics (MD) simulations. The calculations are performed in the constant pressure-constant temperature ensemble, using an algorithm that is able to reproduce structural phase transitions.

Introduction:

Elemental sulfur shows a rich variety of molecular forms and therefore of chemical and physical properties in the crystalline and liquid phases. Recently, a high pressure superconductor transition has been found, with $T_c=17$K (at 162GPa), the highest known for any elemental solid. Natural sulfur is of relevance in geophysics, astrophysics, material sciences and also of massive industrial use. Nevertheless, the complex phase diagram and properties of its condensed phases are far from well known.

The most stable sulfur allotrope at ambient temperature and pressure (STP) is S$_8$, a crown-shaped cyclic S$_8$ molecule, stable in solid, liquid and gas phases.
Orthorhombic $\alpha$-S$_8$ is the crystalline form stable at STP. Figs 1a shows its “crankshaft” structure with four molecules in the primitive unit cell. The space group is $D_{2h}^{4}$ (Fddd), with 16 molecules in this non-primitive orthorhombic cell. If $\alpha$-S$_8$ is slowly heated, it shows a phase transition to monoclinic $\beta$-S$_8$ at 369K (Fig. 1b), which melts at 393K\textsuperscript{1}. Nevertheless, most $\alpha$-S$_8$ crystals do no easily convert to $\beta$-S$_8$, they melt, instead, at 385.8K\textsuperscript{1,2}. $\beta$-S$_8$ is a monoclinic crystal, with six molecules in the primitive unit cell, two of them orientationally disordered\textsuperscript{4,5}. A third crystalline allotrope has been observed: $\gamma$-S$_8$ (Fig. 1c), that can be obtained from solutions of S$_8$ or from its melt\textsuperscript{1,2}. The space group is $C_{2h}^{4}$ (P2/c), with four molecules in the pseudo-hexagonal closed-packed unit cell\textsuperscript{6}. The density of this allotrope, at STP, is 5.8 % higher than that of $\alpha$-S$_8$.

In spite of its relevance, calculations on the crystalline phase diagram of elemental sulfur molecules are scarce. Previous molecular dynamics (MD) simulations of crystalline S$_8$ were limited to constant-volume simulations at normal pressure and temperatures of $\alpha$-S$_8$\textsuperscript{7}, with the only aim to study the intramolecular frequencies obtained by Raman and ir. measurements. The same scope was followed by numerous works that measured crystalline frequencies and performed calculations based on lattice dynamics sums in different approximations\textsuperscript{8}. No attempt to reproduce the phase diagram of this molecule, including determination of crystalline structures, lattice dynamics, or thermodynamic properties of $\beta$- and $\gamma$-S$_8$ as a function of temperature was intended. Here we study the phase diagram of S$_8$ crystals, as given by a simple model of a flexible molecule, by performing a series of constant pressure - constant temperature MD simulations, at several temperatures and zero pressure.

**The inter- and intramolecular potential model:**

The main problem in this type of calculation is the inter- and intramolecular potential model of this flexible molecule. The above mentioned constant volume MD simulations of $\alpha$-S$_8$ were performed with an intermolecular potential model of the atom-atom type, to study the splitting of intramolecular frequencies in a sample of 64 molecules of $\alpha$ -S$_8$\textsuperscript{7}. In our constant temperature - constant pressure MD simulations, these atom-atom parameters are
slightly changed to improve the fit of our results to the experimental unit cell volume and the estimated configurational energy of $\alpha$-S$_8$ at 300K and 0kbar pressure. The parameters of our LJ potential model, for S-S interactions are: $\varepsilon = 1.70 \text{kJ/mol}$ and $\sigma = 3.39 \text{ Å}$.

In a similar way, our intramolecular potential parameters for bending and torsional angles of the flexible S$_8$ molecule are based on those of ref. 7. Our molecule model takes into account all intramolecular modes that mix with lattice modes and can therefore be relevant for structural phase transitions. As calculated in ref. 7 and also measured in all crystalline phases at all temperatures, three main regions are clearly separated in the vibrational spectra: between 10 and $\sim 100 \text{cm}^{-1}$ are found the lattice and torsional modes, between 150 and 250cm$^{-1}$ the bending modes and from 400 to 500cm$^{-1}$ the stretching modes, well above in energies than the rest of vibrational modes. The bond length is therefore held constant at 2.060Å in our calculations. Our flexible molecule model allows, instead, the mixing of the bending and torsional intramolecular motions with lattice modes in a straightforward way. The intramolecular potential for bending angles S-S-S is taken harmonic

$$V(\beta) = \frac{1}{2} C_\beta (\beta - \beta_0)^2,$$

with a force constant of $C_\beta = 25725 \text{ kJ/mol}$ and $\beta_0 = 108 \text{ deg.}$, $k_B$ is the Boltzmann constant. The intramolecular potential for torsion ($\tau$) angles is a double well:

$$V(\tau) = A_\tau + B_\tau \cos(\tau) + C_\tau \cos^2(\tau) + D_\tau \cos^3(\tau),$$

with $A_\tau = 57.192 \text{ kJ/mol}$, $B_\tau = 738.415 \text{ kJ/mol}$, $C_\tau = 2297.880 \text{ kJ/mol}$ and $D_\tau = 557.255 \text{ kJ/mol}$. These parameters describe a double well with minima at $\tau = \pm 98.8 \text{ deg.}$, and a barrier height of about 9kJ/mol at $\tau = 180 \text{ deg.}$ The barrier height at $\tau = 0 \text{ deg.}$ is of 30kJ/mol, out of the range of energies explored in these simulations.

**Calculations:**

The phase diagram and dynamical properties of S$_8$ crystals, as given by this molecular model, are studied in the (N,P,T) ensemble, at zero pressure, by a series of classical MD
simulations. The external pressure is considered isotropic and the MD algorithm allows volume and shape fluctuations of the sample, in order to balance the internal stresses with an external isotropic pressure. The algorithm controls pressure via an extended system which includes as extra variables the MD box parameters. The temperature control of the sample follows the approach of Nose, which also includes an external variable. The equations of motion of these flexible molecules are integrated using the Verlet algorithm for the atomic displacements and the Shake algorithm for the constant bond length constraints on each molecule. The final MD algorithm is totally similar to that used in a study of black Newton films.

As the starting point of our simulations, we considered the available structural data at STP. The molecules were located at the experimental sites, with the measured orientation but with their isolated D4d symmetry. In the course of the simulation, the molecules distort to attain, on a time average, their site symmetry. Following this procedure, the only problem found was with the $\beta$-$S_8$ sample. In this case the calculations were initiated with the LJ parameter $\varepsilon$ multiplied by a factor that in a few (about 100) time steps was varied from 0.1 to 1. This procedure allowed the molecule to attain its initial distortion in the volume of the experimental unit cell.

In a first step we stabilized our samples, at the temperatures quoted in Table I, with a constant volume algorithm for 30000 time steps (each one of 0.01ps.). Later on, the runs in the (N,P,T) ensemble were performed by lowering and increasing the temperature (up to 500K) in steps of 25 or 50K. At each point of the phase diagram the samples are stabilized for 20000 to 30000 time steps and measured in the following 10ps. Near the phase transitions the stabilization times were increased several times. The sample of $\alpha$-$S_8$ crystals consisted of 3*3*2 orthorhombic cells, a sample of 288 molecules. Some points of the phase diagram were recalculated with a sample of 4*4*2 cells (512 molecules). The sample of $\beta$-$S_8$ crystals consisted of 4*4*4 cells (384 molecules) and that of $\gamma$-$S_8$ crystals of 5*3*5 cells (300 molecules).
Results:

a) $\alpha$-$S_8$ crystals:

$\alpha$-$S_8$ crystallizes, at STP, in the orthorhombic space group $F_d$ ($D_{2h}^{24}$) with 16 molecules in a face-centered unit cell, the primitive cell contains 4 molecules at $C_2$ sites. Fig.1a includes part of our sample at 300K and shows the structure in the [110] direction. The molecular rings lie parallel to the crystallographic $c$ axis and are alternately oriented parallel to (110) and (110) crystalline planes. Table I shows the experimental lattice parameters and our calculated values, the largest difference is found in the value of $b$ axis, 2 % larger than its experimental value. The molecular array and their corresponding orientations follows the experimental data. Our calculated configurational energy is -103.5(2)kJ/mol at 300K, from which the heat of sublimation can be estimated as 101.0kJ/mol and compares well with a measured value of 101.8(2)kJ/mol\cite{17}. Also our calculated pair distribution function $g_2(r)$, not included here, compares well with neutron measurements of crystalline $\alpha$-$S_8$ at 300K\cite{18}.

Fig. 2 shows, for $\alpha$, $\beta$- and $\gamma$ - $S_8$, the calculated configurational energy and volume per molecule as a function of temperature. Our simulations reproduce the experimental data of the three crystals at STP. Unfortunately, our $\alpha$-$S_8$ sample of 288 molecules turns out to be unstable for $T \leq 200K$, and distorts to a monoclinic cell, with molecular locations and orientations closely resembling those of $\alpha$-$S_8$. This result was later on confirmed with a larger sample of 512 molecules (4*4*2 orthorhombic cells). Below 200K this large sample does not distort to monoclinic, but nevertheless its configurational energy is higher, and its volume per molecule is larger, than those calculated for the sample of 288 molecules. Also, the fluctuations of the energy and volume, of the sample of 512 molecules, are larger for $T \leq 200$ than their value at 200K.

The coincidence of the calculated distortion at 200K and the experimental fact that crystals of pure $S_8$ are greenish-yellow at 293K and turn white below 193K, made us review the experimental data on this phase. Usually the reference quoted for lattice parameters as a function of temperature is ref\cite{19}. These values were obtained using X-ray powder diffractometry, on different samples and using only three lines. Our calculated powder diffraction
patterns, not included here, were similar for the orthorhombic and monoclinic samples and the scarce experimental data could be not enough to detect the changes. Nevertheless, there is a careful single crystal determination of the structure of α-S₈ at 300 and 100K, where the crystalline charge distribution is measured. This study clearly disregard any possible structural phase transition and shows that the simple molecule model, in spite of the amount of experimental data that it is able to reproduce, should still be improved.

a) β-S₈ crystals:

If α-S₈ is slowly heated, it shows a phase transition to monoclinic β-S₈ at 369K, which melts at 393K. The structure has been determined from single crystal data at room temperature; this was possible because, after annealing at 383K, the crystals may be maintained at 300K for up to a month. The space group is C\textsubscript{2h} (P2\textsubscript{1}/c), with six molecules per unit cell. Four of the molecules are located at general positions: \( \pm (x,y,z; x,1/2-y,1/2+z) \) with \( x=0.367, y=0.356 \) and \( z=0.072 \). The other two molecules (5 and 6) are located at inversion centers: (0,0,0) and (0,1/2,1/2), achieving this symmetry by orientational disorder. Should the disorder be static, the averaged symmetry is over all molecules at inversion sites, if the disorder is dynamic, the molecules achieve its site symmetry on a time average. In both cases the disordered array has a residual entropy of \( k_B/3 \ln 2 \) per molecule. The experimental and lattice parameters of our sample are included in Table I, the molecular orientations are as measured in ref. Fig. 2 includes the calculated configurational energy and volume per molecule, that show no discontinuities as a function of temperature. Instead, we find that the reorientation of molecules 5 and 6 freezes at low temperatures. This is in accord with heat capacity measurements that locate an order-disorder transition transition at 198K. Fig. 1b shows our calculated sample at T=150K, the molecules 5 and 6 are now related by a C\textsubscript{2} symmetry axes.

We find that the orientational disorder of molecules at (0,0,0) and (1/2,1/2,1/2), at high temperatures, is of the dynamical type. Fig. 3 shows the calculated self correlational func-
tions for reorientation of the three inertial molecular axes at 370K. The axis perpendicular
to the molecular plane librates around its equilibrium orientation (z axis in Fig.3), whilst
the molecule reorientates within the plane. The decay time is about 10ps. Furthermore, a
histogram of molecular orientations, averaged over all molecules and all time steps, shows
that the initial correlation has been totally lost after 20000 equilibration time steps. For
$T \leq 150K$ we measure librations of the three axes (with larger amplitudes within the plane),
but no reorientational diffusion.

a) $\gamma$-$S_8$ crystals:

$\gamma$-$S_8$ crystals can be grown from solutions. The crystal is monoclinic, space group $C_{2h}^4$
(P2/c), with four molecules per unit cell. This pseudo-hexagonal structure is denser than
that of $\alpha$-$S_8$, at the same temperature. Our simulations reproduce this structure (Fig.
1c), and Fig. 2 shows that at all temperatures this packing has the higher density. Our
calculated parameters and experimental data, at 300K, are included in Table I. It must be
noticed that the experimental density, measured at 300K, is 2.19$\text{gr/cm}^3$, 5.8% higher than
that of $\alpha$-$S_8$. Nevertheless, in ref. the X-ray measurement determines a structure with
volume per molecule higher than that of $\alpha$-$S_8$, implying a 2.3% lower density. It could be
possible that the temperature of the of the X-ray measurement was higher than 300K.
No other experimental data are available for further comparisons. For this sample we find a
large discontinuity in lattice parameters for $T \geq 400K$ and molecular diffusion for $T \geq 470K$.

d) Phase transitions and the liquid phase:

There is experimental evidence that the phase transitions are obtained when defects are
present, if they are not, metastable states can be maintained for days. Our calculations
do not reproduce the $\alpha$-$\beta$ transition, but this fact corresponds with the experimental evidence
that $\beta$-$S_8$ crystals are more easily grown from the melt and not by increasing temperature
of an $\alpha$-$S_8$ sample.

The same evidence exists for the solid-liquid phase transitions. In this case, the exper-
imental data show that the disorder is generated because $S_8$ molecules start to dissociate when the temperature of the sample is near the melting point.

At even higher temperatures (460K) liquid sulfur is known for its liquid-liquid phase transition, due to changes in the molecular composition of the elemental sulfur molecules $S_n$.

That the disorder is essential to promote the solid-liquid phase transition can be checked by simulating a liquid sample of $S_8$ molecules. These simulations should be valid for temperatures above and near the transition, when the fraction of broken molecules is small. A cubic sample of 216 disordered molecules was studied in the range 350-450K, following the same procedure as the other samples. In this case the MD algorithm allowed changes in the volume of the MD box, but not in its shape. Fig. 4 shows the calculated discontinuity in the configurational energy and volume per molecule at 400K, near that measured for $\alpha$ (386K) and $\beta$ (393K) crystals. For $T\geq 400K$ the sample is liquid, as can be measured by its diffusion constant. Comparison of Figs. 2 and 4 show that the solid - liquid transition is found if the sample is disordered.

Conclusions:

In this paper we study the phase diagram of $S_8$ crystals, at 0kbar pressure, as given by a simple and flexible molecule model. Our calculations can be also considered a model study of cyclo-chain molecules with a torsional potential of a double well type, at difference with hydrocarbon chains which show a triple well torsional potential.

It has to be emphasized that this phase diagram is extremely complex and there are no previous calculations on it. The proposed molecular model is extremely simple but, nevertheless, it gives very good account of many experimental facts. The three crystalline phases are stables. The molecular model reproduces the structure, configurational energy and dynamics of $\alpha$-$S_8$, $\beta$-$S_8$ and $\gamma$-$S_8$ crystals for $T\geq 200K$. At STP the experimental volume per molecule, lattice parameters and molecular array of the three phases compare well with the experimental data, including the smallest volumen per molecule for $\gamma$-$S_8$ crystals.
The calculations also reproduce the orientationally disordered phase of $\beta$-S$_8$, that we determine as dynamically disordered. At low temperatures we calculate a stable orientationally ordered phase.

The solid-liquid phase transition is found near the experimental value, but only for a disordered sample. The $\alpha$- $\beta$-S$_8$ phase transition is not reproduced by either of our two samples. Both facts are in accord with the experimental evidence that the transitions are promoted by disorder\(^2\), if not, metastable states can be maintained for days.

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**Table I**: Experimental and calculated lattice parameters: a, b, c (Å) and monoclinic angle $\beta$ (deg.). Z is the number of molecules in the cell, $V$ (Å$^3$) is the volume per molecule. See the text for a discussion about the $\gamma$-S$_8$ data.

| Phases   | Z  | a(Å)             | b(Å)             | c(Å)             | $\beta$ (deg.) | V(Å$^3$)       |
|----------|----|------------------|------------------|------------------|----------------|----------------|
| $\alpha$-S$_8$ | Ref | 16  | 10.4646(1) | 12.8660(1) | 24.4860(3) | -          | 206.046(98)   |
| (T=300 K) Calc. |     | 10.34(10) | 13.20(3)   | 24.32(7)      | -              | 207.3(1.0)    |
| $\beta$-S$_8$  | Ref | 6   | 10.778     | 10.844        | 10.924         | 95.8$^\circ$  | 211.70        |
| (T=370 K) Calc. |     | 11.01(11) | 10.753(27) | 10.79(10)     | 97.48(07)$^\circ$ | 211.30(74)  |
| $\gamma$-S$_8$ | Ref | 4   | 8.442(30)  | 13.025(10)   | 9.356(50)      | 124.98(30)$^\circ$ | 210.8(1.3) |
| (T=300 K) Calc. |     | 8.03(13) | 13.16(14)  | 8.88(11)     | 120(3)$^\circ$ | 202.5(2.5)    |
Figures:

Fig. 1: Our calculated crystals: a) orthorhombic $\alpha$-S$_8$ at 300K, b) monoclinic $\beta$-S$_8$ at 150K, c) pseudo-hexagonal $\gamma$-S$_8$ at 300K.

Fig. 2: Calculated configurational energy and volume per molecule as a function of temperature for all calculated samples. The lines are a guide to the eyes.

Fig. 3: $\beta$-S$_8$ crystals at 370K: Reorientational self-correlation functions $C_{20}$ for the inertial axes of the two molecules at inversion sites.

Fig. 4: Phase diagram of a disordered cubic sample, with the same scale of Fig. 2. For $T \geq 400$K, the sample is liquid.
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Results:

a) $\alpha$-S$_8$ crystals:

$\alpha$-S$_8$ crystallizes, at STP, in the orthorhombic space group $F_d$ ($D_2^{24}$) with 16 molecules in a face-centered unit cell, the primitive cell contains 4 molecules at $C_2$ sites. Fig. 1a includes part of our sample at 300K and shows the structure in the [110] direction. The molecular rings lie parallel to the crystallographic $c$ axis and are alternately oriented parallel to (110) and (110) crystalline planes. Table I shows the experimental lattice parameters and our calculated values, the largest difference is found in the value of $b$ axis, 2% larger than its experimental value. The molecular array and their corresponding orientations follows the experimental data. Our calculated configurational energy is -103.5(2)kJ/mol at 300K, from which the heat of sublimation can be estimated as 101.0kJ/mol and compares well with a measured value of 101.8(2)kJ/mol$^{17}$. Also our calculated pair distribution function $g_2(r)$, not included here, compares well with neutron measurements of crystalline $\alpha$-S$_8$ at 300K$^{18}$.

Fig. 2 shows, for $\alpha$-, $\beta$- and $\gamma$-S$_8$, the calculated configurational energy and volume per molecule as a function of temperature. Our simulations reproduce the experimental data of the three crystals at STP. Unfortunately, our $\alpha$-S$_8$ sample of 288 molecules turns out to be unstable for $T \leq 200K$, and distorts to a monoclinic cell, with molecular locations and orientations closely resembling that of $\alpha$-S$_8$. This result was later on confirmed with a larger sample of 512 molecules ($4\times4\times2$ orthorhombic cells). Below 200K this large sample do not distort to monoclinic, but nevertheless its configurational energy is higher, and its volume per molecule is larger, than those calculated for the sample of 288 molecules. Also the fluctuations of the energy and volume, of the sample of 512 molecules, are larger for $T \leq 200$ than their value at 200K.

The coincidence of the calculated distortion at 200K and the experimental fact that crystals of pure S$_8$ are greenish-yellow at 293K and turn white below 193K, made us review the experimental data on this phase. Usually the reference quoted for lattice parameters as a function of temperature is ref.$^{19}$. These values were obtained using X-ray powder diffraction, on different samples and using only three lines. Our calculated powder diffraction
patterns, not included here, were similar for the orthorhombic and monoclinic samples and the scarce experimental data could be not enough to detect the changes. Nevertheless, there is a careful single crystal determination of the structure of $\alpha$-S$_8$ at 300 and 100K$^{20}$, where the crystalline charge distribution is measured. This study clearly disregard any possible structural phase transition and shows that the simple molecule model, in spite of the amount of experimental data that is able to reproduce, should still be improved.

a) $\beta$-S$_8$ crystals:

If $\alpha$-S$_8$ is slowly heated, it shows a phase transition to monoclinic $\beta$-S$_8$ at 369K, which melts at 393K$^1$. The structure has been determined from single crystal data$^5$ at room temperature; this was possible because, after annealing at 383K, the crystals may be maintained at 300K for up to a month. The space group is $C_2^5$ ($P2_1/c$), with six molecules per unit cell. Four of the molecules are located at general positions: $\frac{1}{2}(x,y,z; x,1/2-y,1/2+z)$ with $x=0.367$, $y=0.356$ and $z=0.072$. The other two molecules (5 and 6) are located at inversion centers: $(0,0,0)$ and $(0,1/2,1/2)$, achieving this symmetry by orientational disorder. Should the disorder be static, the averaged symmetry is over all molecules at inversion sites, if the disorder is dynamic, the molecules achieve its site symmetry on a time average. In both cases the disordered array has a residual entropy of $k_B/3 \ln 2$ per molecule$^5$. The experimental and lattice parameters of our sample are included in Table I, the molecular orientations are as measured in ref.$^5$.

Fig. 2 includes the calculated configurational energy and volume per molecule, that show no discontinuities as a function of temperature. Instead, we find that the reorientation of molecules 5 and 6 freezes at low temperatures. This is in accord with heat capacity measurements that locate an order-disorder transition transition at 198K$^4$. Fig. 1b shows our calculated sample at $T=150K$, the molecules 5 and 6 are now related by a C2 symmetry axes.

We find that the orientational disorder of molecules at $(0,0,0)$ and $(1/2,1/2,1/2)$, at high temperatures, is of the dynamical type. Fig. 3 shows the calculated self correlational func-
tions for reorientation of the three inertial molecular axes at 370K. The axis perpendicular to the molecular plane librates around its equilibrium orientation (z axis in Fig.3), whilst the molecule reorientates within the plane. The decay time is about 10ps. Furthermore, a histogram of molecular orientations, averaged over all molecules and all time steps, shows that the initial correlation has been totally lost after 20000 equilibration time steps. For $T \leq 150K$ we measure librations of the three axes (with larger amplitudes within the plane), but no reorientational diffusion.

a) $\gamma$-S$_8$ crystals:

$\gamma$-S$_8$ crystals can be grown from solutions$^{1,2}$. The crystal is monoclinic, space group $C_{2h}^4$ (P2/c), with four molecules per unit cell$^6$. This pseudo-hexagonal structure is denser than that of $\alpha$-S$_8$, at the same temperature$^{2,6}$. Our simulations reproduce this structure (Fig. 1c), and Fig. 2 shows that at all temperatures this packing has the higher density. Our calculated parameters and experimental data, at 300K, are included in Table I. It must be noticed that the experimental density, measured at 300K, is 2.19gr/cm$^3$, 5.8% higher than that of $\alpha$-S$_8$. Nevertheless, in ref.$^6$ the X-ray measurement determines a structure with volume per molecule higher than that of $\alpha$-S$_8$, implying a 2.3% lower density. It could be possible that the temperature of the of the X-ray measurement was higher than 300K.

No other experimental data is available for further comparisons. For this sample we find a large discontinuity in lattice parameters for $T \geq 400K$ and molecular diffusion for $T \geq 470K$.

d) Phase transitions and the liquid phase:

There is experimental evidence that the phase transitions are obtained when defects are present, if they are not, metastable states can be maintained for days$^{1,2,5}$. Our calculations do not reproduce the $\alpha$-$\beta$ transition, but this fact corresponds with the experimental evidence that $\beta$-S$_8$ crystals are more easily grown from the melt and not by increasing temperature of an $\alpha$-S$_8$ sample.

The same evidence exists for the solid-liquid phase transitions. In this case, the exper-
Experimental data shows that the disorder is generated because S₈ molecules start to dissociate when the temperature of the sample is near the melting point. At even higher temperatures (460K) liquid sulfur is known for its liquid-liquid phase transition, due to changes in the molecular composition of the elemental sulfur molecules S₈.

That the disorder is essential to promote the solid-liquid phase transition can be checked by simulating a liquid sample of S₈ molecules. These simulations should be valid for temperatures above and near the transition, when the fraction of broken molecules is small. A cubic sample of 216 disordered molecules was studied in the range 350-450K, following the same procedure as the other samples. In this case the MD algorithm allowed changes in the volume of the MD box, but not in its shape. Fig. 4 shows the calculated discontinuity in the configurational energy and volume per molecule at 400K, near that measured for α (386K) and β (393K) crystals. For T≥400K the sample is liquid, as can be measured by its diffusion constant. Comparison of Figs. 2 and 4 show that the solid - liquid transition is found if the sample is disordered.

Conclusions:

In this paper we study the phase diagram of S₈ crystals, at 0kbar pressure, as given by a simple and flexible molecule model. Our calculations can be also considered a model study of cyclo-chain molecules with a torsional potential of a double well type, at difference with hydrocarbon chains which show a triple well torsional potential.

It has to be emphasized that this phase diagram is extremely complex and there are no previous calculations on it. The proposed molecular model is extremely simple but, nevertheless, it gives very good account of many experimental facts. The three crystalline phases are stables. The molecular model reproduces the structure, configurational energy and dynamics of α-S₈, β-S₈ and γ-S₈ crystals for T≥200K. At STP the experimental volume per molecule, lattice parameters and molecular array of the three phases compare well with the experimental data, including the smallest volumen per molecule for γ-S₈ crystals.
The calculations also reproduce the orientationally disordered phase of $\beta$-S$_8$, that we determine as dynamically disordered. At low temperatures we calculate a stable orientationally ordered phase.

The solid-liquid phase transition is found near the experimental value, but only for a disordered sample. The $\alpha$-$\beta$-S$_8$ phase transition is not reproduced by any of our two samples. Both facts are in accord with the experimental evidence that the transitions are promoted by disorder$^2$, if not, metastable states can be maintained for days.

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**Table I:** Experimental and calculated lattice parameters: a, b, c (Å) and monoclinic angle β (deg.). Z is the number of molecules in the cell, V (Å³) is the volume per molecule. See the text for a discussion about the γ-S₈ data.

| Phases | Z | a(Å)       | b(Å)     | c(Å)       | β (deg.) | V(Å³)       |
|--------|---|------------|----------|------------|----------|-------------|
| α-S₈   |   | 10.4646(1) | 12.8660(1)| 24.4860(3)| -        | 206.046(98) |
| (T=300 K) Calc. | 10.34(10) | 13.20(3)   | 24.32(7)  | -         | 207.3(1.0) |
| β-S₈   |   | 10.778     | 10.844    | 10.924     | 95.8°    | 211.70      |
| (T=370 K) Calc. | 11.01(11) | 10.753(27) | 10.79(10) | 97.48(07)°| 211.30(74) |
| γ-S₈   |   | 8.442(30)  | 13.025(10)| 9.356(50) | 124.98(30)°| 210.8(1.3) |
| (T=300 K) Calc. | 8.03(13) | 13.16(14) | 8.88(11) | 120(3)°  | 202.5(2.5) |
Figures:

Fig. 1: Our calculated crystals: a) orthorhombic $\alpha$-$S_8$ at 300K, b) monoclinic $\beta$-$S_8$ at 150K, c) pseudo-hexagonal $\gamma$-$S_8$ at 300K.

Fig. 2: Calculated configurational energy and volume per molecule as a function of temperature for all calculated samples. The lines are a guide to the eyes.

Fig. 3: $\beta$-$S_8$ crystals at 370K: Reorientational self-correlation functions $C_{20}$ for the inertial axes of the two molecules at inversion sites.

Fig. 4: Phase diagram of a disordered cubic sample, with the same scale of Fig. 2. For $T \geq 400$K, the sample is liquid.