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Molecular dynamics simulation on the morphology of 1,1-diamino-2,2-dinitroethylene (FOX-7) affected by dimethyl sulfoxide (DMSO) and temperature

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Abstract: Attachment energy (AE) model is adopted to research the influence of dimethyl sulfoxide (DMSO) and temperature on the crystal morphology of 1,1-diamino-2,2-dinitroethylene (FOX-7). FOX-7 crystal habits in DMSO at different temperatures simulated by AE model have apparently changed compared with the vacuum morphology, indicating that the solvent and temperature can affect FOX-7 morphology. Moreover, the influence of model dimension on the attachment energy has been studied, and a reasonable model size is obtained based on the model dimension study results. Besides, the radial distribution function analysis shows that the solvent molecules adsorb on the FOX-7 surfaces mainly via the solvent-crystal interface interactions of van der Waals forces (vdW) and Coulomb interactions. The analysis of diffusion coefficient of DMSO molecules on the crystal growth surfaces shows that the growth habit is also influenced by the diffusion capacity of DMSO molecules. These simulation results of this study can provide some guidance for the crystallization process of FOX-7.

Keywords: FOX-7; molecular dynamics simulation; DMSO; temperature effect; crystal morphology

Introduction

1,1-Diamino-2,2-dinitroethylene (FOX-7), with combined high detonation velocity (approaching to hexogon, RDX) and low sensitivity (close to 1,3,5-triamino-2,4,6-trinitrobenzene, TATB), is a considerable explosive ingredient with significant potential for application in high-performance, insensitive munition-compliant explosive compositions. In general, the crystal size and morphology of FOX-7 are controlled by various recrystallization techniques such as evaporation crystallization and cooling crystallization, which can considerably affect the final performance and sensitivity.¹⁻³ Compared with needle-shaped crystals, spherical crystals can improve the packing density and decrease the mechanical sensitivities largely.⁴ Thus, researching into the FOX-7 crystal morphology is of important practical significance. The morphology of explosive is governed by both the internal structure and the external

conditions such as solvent ⁵, temperature, additive and crystal technology ⁶, among which solvent and temperature have been found to be critical external factors determining the relative growth rate and consequently the crystal habit ^{7, 8}.

Currently, molecular modelling techniques, with low-cost and security, on the prediction of crystal shape have been extensively developed. ⁹⁻¹² In particular, the molecular dynamics (MD) simulation which can provide atomic-scale information becomes a powerful one of these techniques. ¹³ Therefore, the MD simulation method is used to study the dimethyl sulfoxide (DMSO) and temperature effect on the morphology of FOX-7. According to the previous studies, the corrected attachment energy model was adopted to simulate the morphology of FOX-7 in DMSO with the temperature ranging from 298 to 343 K by Materials Studio (MS) 6.0 software. In addition, we also performed the diffusion coefficient calculation of DMSO molecules on the habit crystal faces to probe the effect of solvent on the morphology of FOX-7.

So far molecular modelling techniques on the prediction of crystal shape have been an active research topic. Many researchers adopt attachment energy (AE) model to study the influence of solvent or additive on the crystal morphology ^{14, 15}, and most of them extend a single crystal surface to a 3×3×3 supercell to calculate the solvent-effect attachment energy ¹⁶⁻¹⁸. However, 3×3×3 supercell is not a universal size, and the accuracy of this size is low for many crystallographic planes. What's more, there is no unified standard for the number of solvent molecules which is an important parameter for the morphology simulation in the fixed model. In this study, we systematically investigated the influence of supercell crystal length, width, thickness and the amount of solvent on the attachment energy. Based on the research results, a reasonable size of solvent/crystal surface double layer model was proposed. The method can be applied to other crystal morphology study. When the model size is confirmed, we could predict the morphology of FOX-7 in different systems.

Computational theory and details

Computational theory

Based on period bond chain (PBC) theory, Hartman and Bennema proposed the AE model to predict crystal vacuum morphology.^{19, 20} The attachment energy, E_{att} , is defined as the energy release per growth slice upon adding a surface layer of one slice thickness d_{hkl} onto the corresponding crystal surface²¹, which can be calculated as follows:

$$(1) \quad E_{\text{att}} = E_{\text{latt}} - E_{\text{slice}}$$

where E_{latt} stands for the lattice energy of the crystal. E_{slice} represents the energy of a growth slice of thickness d_{hkl} .

The relative growth rate of an $(h \ k \ l)$ face in a vacuum, R_{hkl} , is assumed to be proportional to the absolute value of the attachment energy of the corresponding crystal surface:

$$(2) \quad R_{\text{hkl}} \propto |E_{\text{att}}|$$

However, most crystals are grown from solvent which affects the growth rate of crystal surfaces. Because the solvent molecules must be removed from the surface before the crystal faces can grow. This costs energy and herewith the apparent attachment energy decreases. To predict the impact of solvent on the crystal morphology, an energy correction term E_{S} for the vacuum attachment energy E_{att} should be introduced to represent this solvent effect. The modified attachment energy, $E_{\text{att}}^{\text{S}}$, can be calculated as follows:

$$(3) \quad E_{\text{att}}^{\text{S}} = E_{\text{att}} - E_{\text{S}}$$

Then the relative growth rate of each surface ($R_{\text{hkl}}^{\text{S}}$) in solvent is taken to be proportional to the absolute value of $E_{\text{att}}^{\text{S}}$ ^{17, 18}:

$$(4) \quad R_{\text{hkl}}^{\text{S}} \propto |E_{\text{att}}^{\text{S}}|$$

Therefore, the calculation of energy correction term E_{S} is the key step for the simulation of the crystal habit. Here, E_{S} represents the energy of solvent binding on the crystal surface $(h \ k \ l)$, which can be calculated by the following formula:

$$(5) \quad E_{\text{S}} = \frac{E_{\text{int}} \times A_{\text{acc}}}{A_{\text{box}}}$$

where A_{acc} is the solvent-accessible area of the crystal surface which achieved by

calculating the Connolly surface using Atom Volumes & Surfaces tool of MS. A_{box} is the total crystal face area of the simulated model along the $(h\ k\ l)$ plane. E_{int} represents the interaction energy between the solvent layer and crystal face, and it can be calculated using the following formula:

$$(6) \quad E_{\text{int}} = E_{\text{tot}} - E_{\text{sur}} - E_{\text{sol}}$$

where E_{tot} is the total energy of the solvent layer and crystal face. E_{sur} is the energy of the crystal surface without the solvent layer. E_{sol} is the energy of the solvent layer without the crystal face.

Simulation details

The crystal structure of FOX-7 with space group $P2_1/n$, $Z = 4$, $a = 6.94\ \text{\AA}$, $b = 6.64\ \text{\AA}$, $c = 11.34\ \text{\AA}$, $\beta = 90.6^\circ$ are displayed in Fig. 1. All the geometry of the unit lattices was optimized by Conjugate gradient algorithm in the COMPASS force field which had been parameterized and validated by condensed phase properties.¹⁸ The comparison between experimental lattice parameters and the optimized values of FOX-7 is listed in Table 1. The results illustrate that the optimized lattice parameters deviate from the experimental values within 7%, which demonstrates that the COMPASS force field is suitable for the simulation of FOX-7.

Fig. 1. The crystal structure of FOX-7.

Table 1. The comparison of the experimental and optimized lattice parameters of FOX-7.

Lattice parameter	$a/\text{\AA}$	$b/\text{\AA}$	$c/\text{\AA}$	$\beta/^\circ$
Experimental	6.94	6.64	11.34	90.60
Computational	6.46	6.37	11.92	90.74

Relative error/%	-6.92	-4.07	5.11	0.15
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Subsequently, the AE model was selected to predict the crystal morphology of FOX-7 in vacuum, which gave a list of morphologically possible growth faces. Then the FOX-7 crystal was cleaved along these six morphologically significance surfaces and extended to 3D periodic supercell. Next, a solvent amorphous cell whose lengths and widths were based on the FOX-7 supercell, and the thicknesses were adjusted by the amount of the solvent molecules was built. To investigate the effect of solvent and temperature on the morphology, the interfacial model was established, which was composed of a FOX-7 crystal layer and a DMSO solvent layer. The procedure of model establishment of the six main faces is displayed in Fig. 2.

Fig. 2. The procedure of model establishment of the main faces of FOX-7.

In this work, all computation simulations adopted Forcite Module to perform the molecular dynamic simulation for 400 ps with NVT ensemble, COMPASS²² force field at the temperature of 298 K under the Andersen thermostat²³. Standard Ewald method with an accuracy of 0.0001 kcal·mol⁻¹ was employed to simulate the electrostatic interactions, and the van der Waals forces were simulated by utilizing atom-based method with a cutoff distance (d_c) of 15.5 Å²⁴.

Results and Discussions

FOX-7 crystal morphology in Vacuum

We simulate the vacuum morphology of FOX-7 with six dominant surfaces by the AE model, which is in a gem shape with an aspect ratio of 1.58, as shown in Fig. 3(a). The molecular interactions between FOX-7 molecules calculated by morphology and visualized by crystal graph are shown in Fig. 3(b), which demonstrates that the stronger the molecular force is, the faster the crystal grows.^{10, 11} In Fig. 3(b), the blue lines

represent strong interaction while red lines represent weak interaction, which indicates that FOX-7 grows faster along the blue lines direction than the red lines direction. Based on the periodic bond chain (PBC) theory, the fastest growing direction is the strongest bond direction. The surfaces with fast growth rate will disappear and the surfaces with slow growth rate will appear on the final morphology, which results in the morphology domination of FOX-7 crystal in vacuum with six faces. Table 2 lists the relevant parameters of the six significant faces $\{0\ 1\ 1\}$, $\{1\ 0\ -1\}$, $\{1\ 0\ 1\}$, $\{0\ 0\ 1\}$, $\{1\ 1\ -1\}$ and $\{1\ 1\ 0\}$, among which the $\{0\ 1\ 1\}$ face possesses the strongest morphological importance because of the largest total habit facet area percentage 37.05%. On the contrary, the $\{1\ 1\ 0\}$ face has the lowest morphological importance with $S\%$ of 4.18%.

Table 2. The parameter of the main crystal faces of FOX-7.

$\{h\ k\ l\}$	Multiplicity	$d_{hkl}/\text{\AA}$	$A_{hkl}/\text{\AA}^2$	$E_{\text{att}}(\text{Total})/\text{kcal}\cdot\text{mol}^{-1}$	$S\%$
$\{0\ 1\ 1\}$	4	5.62	87.33	-44.06	37.05
$\{1\ 0\ -1\}$	2	5.71	85.95	-40.23	21.74
$\{1\ 0\ 1\}$	2	5.65	86.89	-51.97	13.71
$\{0\ 0\ 1\}$	2	5.96	41.16	-50.10	13.10
$\{1\ 1\ -1\}$	4	4.25	115.41	-48.54	10.16
$\{1\ 1\ 0\}$	4	4.54	108.20	-54.44	4.18

Fig. 3. **a** Crystal morphology and **b** molecular interaction of FOX-7 in vacuum predicted by AE model.

In order to understand the interactions between solvent molecules and different FOX-7 crystal surfaces, the molecular packing structures of FOX-7 are displayed in Fig. 4, and the blue grid on the FOX-7 crystal surface stands for the accessible solvent surface. The A_{acc} , surface area (A_{hkl}) and corresponding $A_{\text{acc}}/A_{\text{hkl}}$ value of different FOX-7 habit surfaces are displayed in Table 3. Based on the simulation, the molecular arrangement of FOX-7 morphologically significance surfaces illustrate the surface properties intuitively. Plainly, the molecular arrangement of $\{0\ 1\ 1\}$, $\{0\ 0\ 1\}$, $\{1\ 1\ 0\}$ and $\{1\ 1\ -1\}$ surfaces are relatively flat on the molecular level while $\{1\ 0\ -1\}$ and $\{1\ 0\ 1\}$ surfaces are uneven with many large voids, which may contribute to solvent molecules adsorption. On the other hand, the value of $A_{\text{acc}}/A_{\text{hkl}}$ is larger, the surface topography is more complex, which is easier to be invaded by solvent molecules. Accordingly, a larger $A_{\text{acc}}/A_{\text{hkl}}$ may result in a larger energy correction term E_s and dramatically influence the final morphology. The exposed atoms of different FOX-7 surface are different, which will have a significant impact on the interaction between FOX-7 surfaces and solvent.

Table 3. The parameter values for the crystal habit surfaces of FOX-7.

	$\{0\ 1\ 1\}$	$\{1\ 0\ -1\}$	$\{1\ 0\ 1\}$	$\{0\ 0\ 1\}$	$\{1\ 1\ -1\}$	$\{1\ 1\ 0\}$
$A_{\text{acc}}/\text{\AA}^2$	104.00	131.39	124.33	50.08	142.96	143.59
$A_{\text{hkl}}/\text{\AA}^2$	87.33	85.95	86.89	41.16	115.41	108.20
$A_{\text{box}}/\text{\AA}^2$	1309.92	1289.32	1303.30	1028.98	1384.96	1298.37
$A_{\text{acc}}/A_{\text{hkl}}$	1.19	1.53	1.43	1.22	1.24	1.33

Fig. 4. The geometric structures of different FOX-7 planes represented by the Connolly surface

model.

The influence of model size on $E_{\text{att}}^{\text{s}}$

Model dimension is a critical factor that dramatically influences the $E_{\text{att}}^{\text{s}}$ which significantly affects the final predicted morphology. If the model dimension is too small the deviation of the calculated $E_{\text{att}}^{\text{s}}$ will be large, which results in the inaccurate morphology prediction. However, if the model size is too large the simulation time will last long, and the accuracy does not increase too much. Therefore, it's an indispensable step to find a suitable model size to meet the accuracy and consume less time.

In this study, we have systematically investigated the influence of model size on the $E_{\text{att}}^{\text{s}}$. Take {0 1 1} surface of FOX-7 as an example to illustrate the detailed steps of the research. Firstly, we fix the size of FOX-7 supercell and change the amount of the solvent molecules to alter the thickness of the solvent amorphous cell. Secondly, the size of solvent amorphous cell is fixed, and we change the thickness of FOX-7 surface. Thirdly, we fix the thickness of FOX-7 surface and solvent amorphous cell, and the length (U) and width (V) of the FOX-7 surface are changed. At last, we fix the size of FOX-7 supercell and solvent amorphous cell, and the vacuum thickness (t_v) of the interface model are changed. The calculated $E_{\text{att}}^{\text{s}}$ affected by the model size are summarized in Table 4 and Fig. 5.

Table 4. The influence of solvent thickness (t_s), crystal thickness (t_c), vacuum thickness (t_v) and the length (U) and width (V) on $E_{\text{att}}^{\text{s}}$.

	Size/Å	E_{tot} /kcal·mol ⁻¹	E_{surf} /kcal·mol ⁻¹	E_{solv} /kcal·mol ⁻¹	E_{int} /kcal·mol ⁻¹	$E_{\text{att}}^{\text{s}}$ /kcal·mol ⁻¹
t_s	5.40	-48468.61	-47823.53	-379.21	-265.87	-22.95
	10.80	-49032.08	-47809.44	-934.65	-287.98	-21.20
	16.21	-49627.54	-47812.99	-1520.28	-294.26	-20.70
	21.61	-50240.59	-47819.78	-2124.25	-296.56	-20.52
	27.01	-50764.29	-47805.26	-2661.79	-297.24	-20.46
t_c	5.62	-17294.01	-15532.77	-1510.21	-251.02	-24.13
	11.24	-33399.53	-31564.97	-1547.51	-287.05	-21.27

	16.86	-49627.54	-47812.99	-1520.28	-294.26	-20.70
	22.48	-65820.45	-64003.62	-1523.73	-293.09	-20.79
	28.10	-82009.98	-80216.27	-1497.86	-295.85	-20.57
	0.00	-49748.79	-47795.57	-1403.53	-549.70	-0.42
	7.75	-49646.69	-47812.68	-1395.10	-438.90	-9.22
t_v	15.50	-49628.82	-47800.97	-1530.64	-297.21	-20.46
	31.00	-49625.11	-47812.33	-1517.44	-295.34	-20.61
	46.50	-49616.27	-47770.76	-1546.13	-299.38	-20.29
	1U×3V	-9959.18	-9570.87	-339.62	-48.69	-24.73
	2U×3V	-19898.17	-19106.43	-686.22	-105.53	-23.12
	3U×3V	-29914.12	-28712.50	-1035.62	-166.00	-22.10
U	4U×3V	-39850.10	-38214.76	-1406.03	-229.30	-21.30
	5U×3V	-49627.54	-47812.99	-1520.28	-294.26	-20.70
	6U×3V	-59742.07	-57307.09	-2082.88	-352.10	-20.77
	7U×3V	-69849.28	-66974.97	-2459.51	-414.81	-20.54
	5U×1V	-16517.53	-15901.28	-535.13	-81.12	-24.74
	5U×2V	-33047.21	-31869.15	-989.65	-188.42	-21.62
V	5U×3V	-49627.54	-47812.99	-1520.28	-294.26	-20.70
	5U×4V	-66204.66	-63765.03	-2047.08	-392.54	-20.69
	5U×5V	-82654.31	-79647.28	-2513.49	-493.53	-20.55

Fig. 5. The influence of model size on E_{att}^S .

The simulation results manifest that with the increase of the model size, the E_{att}^S

growth increases rapidly initially and then remains approximately constant. The researches of the influence of the solvent thickness (t_s) and crystal thickness (t_c) on the E_{att}^s reveal that, when t_s and t_c are less than the cutoff distance (d_c) of vdW forces, the E_{att}^s increases quickly, but when t_s and t_c are greater than d_c , the E_{att}^s almost not changed. Thus, we should build a model with t_s and t_c no less than d_c , or the accuracy will be low, and it is all completely unnecessary to build a model of large t_s and t_c , because the precision can't be improved remarkably and the simulation time will last long. The study of the influence of vacuum thickness (t_v) shows that, with the increase of t_v , the E_{att}^s decreases rapidly initially and then remains approximately constant. When t_v is larger than d_c , the E_{att}^s almost not changed, which indicates that we need build a model with t_v no less than d_c . The investigation of the influence of crystal area on the E_{att}^s demonstrates that, when the length and width of the supercell are less than $2d_c$, the E_{att}^s grows with the increase of the length and width, when the length and width are larger than $2d_c$, the E_{att}^s almost maintains unchanged. Accordingly, to balance the calculation accuracy and simulation time, we should establish a FOX-7/solvent model with the length and width of the supercell are no less than $2d_c$, and the t_s , t_c and t_v are greater than d_c .

Besides, when we fix the width of the FOX-7 surface, the E_{att}^s grows with the increase of the length, however, when the width reaches three times as initial width, the following E_{att}^s remains almost static. And when the length of the FOX-7 surface is fixed with $5U$, the E_{att}^s increases first and then is almost constant, the width with $3V$ is suitable. So, when the AE model is established, we can't simply build a $3 \times 3 \times 3$ supercell, but an appropriate model size that is based on the above analysis. Based on the research results, the U , V and thickness of the six significant faces $\{0\ 1\ 1\}$, $\{1\ 0\ -1\}$, $\{1\ 0\ 1\}$, $\{0\ 0\ 1\}$, $\{1\ 1\ -1\}$ and $\{1\ 1\ 0\}$ were extended to $5 \times 3 \times 3$, $5 \times 3 \times 3$, $3 \times 5 \times 3$, $5 \times 5 \times 2$, $3 \times 4 \times 4$ and $3 \times 4 \times 4$, respectively.

FOX-7 crystal morphology in DMSO solvent

The morphological significant crystal surface supercells are constructed to study the morphology of FOX-7 in DMSO according to the analysis of the influence of model

size on $E_{\text{att}}^{\text{s}}$.

Compared with the vacuum conditions, the growth of FOX-7 in solution need to remove the solvent adsorbed on the crystal surfaces, which consumes some energy. The consumed energy is the energy correction term E_{s} which can be calculated by the interaction energy between FOX-7 surfaces and solvent molecules. When the E_{s} is obtained, the solvent-effected attachment energy $E_{\text{att}}^{\text{s}}$ can be computed, then the morphology of FOX-7 can be predicted. The simulated interaction energy results and crystal habit properties are summarized in Table 5. The negative interaction energy of each FOX-7/solvent systems indicate that the adsorption of solvent molecules on FOX-7 faces is exothermic and thermodynamically favorable. The predicted morphology of FOX-7 and the experimental FOX-7 morphology affected by DMSO are demonstrated in Fig. 6.

Table 5. Interaction energy and modified attachment energy of FOX-7 faces in DMSO.

$E/\text{kcal}\cdot\text{mol}^{-1}$	{0 1 1}	{1 0 -1}	{1 0 1}	{0 0 1}	{1 1 -1}	{1 1 0}
E_{tot}	-49617.61	-49862.80	-49499.26	-41384.79	-53121.54	-52833.30
E_{sur}	-47824.31	-48074.20	-47706.92	-39971.19	-51118.61	-50997.24
E_{sol}	-1505.59	-1525.62	-1475.21	-1164.92	-1695.54	-1525.41
E_{int}	-287.72	-262.98	-317.14	-248.68	-307.40	-310.65
E_{s}	-22.84	-26.80	-30.25	-12.10	-31.73	-34.35
$E_{\text{att}}^{\text{s}}$	-21.22	-13.43	-21.72	-38.00	-16.81	-20.09
$R_{\text{hkl}}^{\text{s}}$	1.58	1.00	1.62	2.83	1.25	1.50
$S\%$	23.34	28.58	18.46	0.00	22.17	7.45
Aspect ratio ^a	2.79		relative surface/ volume ratio ^b			1.19

Notes: ^a Ratio between the longest and the shortest diameter of the habit. ^b Compares the surface area of the habit with that of a sphere of the same volume.

Fig. 6. Crystal morphology of FOX-7 in DMSO.

Table 5 shows that the aspect ratio of FOX-7 in DMSO with 2.79 is larger than that of FOX-7 in vacuum with 1.58, which reveals the solvent effect on FOX-7 morphology. In DMSO, the descending order of interaction between DMSO solvent and different crystal faces is $\{0\ 0\ 1\} > \{1\ 0\ 1\} > \{0\ 1\ 1\} > \{1\ 1\ 0\} > \{1\ 1\ -1\} > \{1\ 0\ -1\}$ which is different from that in vacuum. This indicates that the solvent effect has brought a significant change in the growth rates of the surfaces. Compared with that in vacuum, the crystal face of $\{0\ 0\ 1\}$ with the largest modified attachment energy has finally disappeared due to the solvent effect.

The influence of temperature on FOX-7 morphology

Temperature is one of the factors that affects the morphology of crystals.⁸ We have performed MD simulations to explain the relationship between the FOX-7 morphology and temperature in DMSO solvent. **Table 6** and **Fig. 7** exhibit the simulated results.

Table 6. Interaction energy and modified attachment energy of FOX-7 faces in DMSO at different temperatures.

T/K	$E/\text{kcal}\cdot\text{mol}^{-1}$	$\{0\ 1\ 1\}$	$\{1\ 0\ -1\}$	$\{1\ 0\ 1\}$	$\{0\ 0\ 1\}$	$\{1\ 1\ -1\}$	$\{1\ 1\ 0\}$
298	E_{tot}	-49617.61	-49862.80	-49499.26	-41384.79	-53121.54	-52833.30

	E_{sur}	-47824.31	-48074.20	-47706.92	-39971.19	-51118.61	-50997.24
	E_{sol}	-1505.59	-1525.62	-1475.21	-1164.92	-1695.54	-1525.41
	E_{int}	-287.72	-262.98	-317.14	-248.68	-307.40	-310.65
	E_{s}	-22.84	-26.80	-30.25	-12.10	-31.73	-34.35
	$E_{\text{att}}^{\text{s}}$	-21.22	-13.43	-21.72	-38.00	-16.81	-20.09
	$S\%$	23.34	28.58	18.46	0.00	22.17	7.45
	Aspect ratio	2.79		relative surface/ volume ratio			1.19
313	E_{tot}	-49361.24	-49647.58	-49269.35	-41171.74	-52846.95	-52623.85
	E_{sur}	-47656.91	-47923.77	-47519.79	-39849.14	-50918.67	-50878.27
	E_{sol}	-1415.97	-1467.62	-1434.45	-1085.27	-1624.10	-1437.77
	E_{int}	-288.35	-256.19	-315.11	-237.33	-304.18	-307.81
	E_{s}	-22.89	-26.11	-30.06	-11.55	-31.40	-34.04
	$E_{\text{att}}^{\text{s}}$	-21.17	-14.12	-21.91	-38.55	-17.14	-20.40
	$S\%$	25.11	27.09	18.56	0.00	22.06	7.17
	Aspect ratio	2.71		relative surface/ volume ratio			1.18
328	E_{tot}	-49105.35	-49337.08	-48849.94	-40966.39	-52581.53	-52397.11
	E_{sur}	-47473.17	-47800.86	-47219.34	-39733.92	-50811.96	-50790.88
	E_{sol}	-1339.53	-1286.20	-1327.45	-1010.15	-1470.10	-1303.21
	E_{int}	-292.65	-250.02	-318.57	-222.31	-299.47	-303.03
	E_{s}	-23.23	-25.48	-30.39	-10.82	-30.91	-33.51
	$E_{\text{att}}^{\text{s}}$	-20.83	-14.75	-21.58	-39.28	-17.63	-20.93
	$S\%$	28.12	26.10	19.25	0.00	20.75	5.78
	Aspect ratio	2.61		relative surface/ volume ratio			1.17
343	E_{tot}	-48856.02	-49124.30	-48644.84	-40834.43	-52275.22	-52072.03
	E_{sur}	-47322.87	-47661.29	-47110.14	-39675.25	-50624.62	-50574.99
	E_{sol}	-1239.38	-1219.29	-1219.97	-949.59	-1358.10	-1199.77
	E_{int}	-293.76	-243.72	-314.72	-209.59	-292.50	-297.28
	E_{s}	-23.32	-24.84	-30.02	-10.20	-30.19	-32.88
	$E_{\text{att}}^{\text{s}}$	-20.74	-15.39	-21.95	-39.90	-18.34	-21.57

Fig. 7. Crystal morphology of FOX-7 in DMSO at different temperatures.

From Table 6, we can see that with an increase of temperature, the aspect ratio of FOX-7 in DMSO decreases gradually while the relative surface/volume ratio is almost unchanged, which indicates that the higher temperature contributes to the sphericity of FOX-7 in DMSO solvent. The relative growth rates of the main six faces are substantially retained due to the almost invariable $|E_{\text{att}}^s|$. In addition, with the increase of temperature, the morphological importance of the $\{0\ 1\ 1\}$ face become the greatest, while that of the $\{1\ 0\ -1\}$, $\{1\ 1\ -1\}$ and $\{1\ 1\ 0\}$ faces diminish because of their weaker DMSO solvent effect. Fig. 7 displays the predicted morphology of FOX-7 in DMSO at different temperatures which is consistent with the corresponding experimental results.

Radial distribution function (RDF) of the interfacial model

Solvent-surface adsorption interactions are essential intermolecular interactions that can be divided into three types, including short-range interactions (hydrogen bonding and vdW interactions) and long-range interactions (Coulomb interactions). Generally, the distance range of hydrogen bonding and vdW interactions is within 3.1 Å and 3.1-5.0 Å¹⁶ respectively, while that of the Coulomb interactions is over 5.0 Å. The RDF, a measure of the possibility of finding a particle at a distance of r away from a given reference particle, is widely used in analyzing the solvent-crystal interactions. The RDF between DMSO and the $\{0\ 1\ 1\}$ face of FOX-7 at 298 K is plotted in Fig. 8.

Fig. 8. Radial distribution function of the interface model of FOX-7 and DMSO.

Fig. 8 shows that the high peaks exist mainly in the range between 2.44 Å and 4.74 Å, among which there is one peak in the distance of 4.74 Å in the curve of FOX-7-H ~ DMSO-S, indicating the existence of vdW interactions between FOX-7-H and DMSO-S. Besides, the other peak with the distance 8.84 Å in this curve indicates that FOX-7-H and DMSO-S is to some extent Coulomb interactions. The peak of each curve within 3.1 Å is very small, and the $g(r)$ is smaller than 0.5, which indicates that the hydrogen bonding does not exist between FOX-7 and DMSO. And there are no obvious peaks in curves of FOX-7-O ~ DMSO-H and FOX-7-N ~ DMSO-H within 5 Å, suggesting that there is no obvious existence of hydrogen bonding and vdW interactions.

The solvent molecules diffusion capacity

According to the prediction of AE model, the predominant face of FOX-7 crystal in DMSO is $\{1\ 0\ -1\}$, which is in agreement with the experimental result. However, the simulation results of the interaction energy between the FOX-7 crystal faces and the solvent shows that the adsorption energy of the solvent on the $\{1\ 0\ 1\}$ face is the largest. Thus, it can be seen that the solvent molecules diffusion capacity also plays a role in the growth of various FOX-7 crystal faces, which involves the diffusion coefficient (D) of solvent molecules on different crystal faces. The D of DMSO molecules on various FOX-7 crystal is calculated using the well-known Einstein diffusion equation. According to the equation, the three-dimensional diffusion coefficient of a molecule

can be evaluated as the derivative of its mean square displacement (MSD) with respect to time as follows ^{13, 16}:

$$(7) \quad D = \frac{1}{6} \lim_{t \rightarrow \infty} \frac{d}{dt} \sum_{i=1}^N \langle |r_i(t) - r_i(0)|^2 \rangle$$

Where r_i denotes the position vector of the particle, and the angular brackets denote an ensemble average. So, the slope of the MSD as a function of time can be used to evaluate the D of a particle undergoing random Brownian motion in three dimensions. Fig. 9 plots the results of the MSD of FOX-7 molecules on {0 1 1}, {1 0 -1}, {1 0 1}, {0 0 1}, {1 1 -1} and {1 1 0} faces at 298 K.

Fig. 9. The MSD of FOX-7 molecules on {0 1 1}, {1 0 -1}, {1 0 1}, {0 0 1}, {1 1 -1} and {1 1 0} faces at 298 K.

The large value of the diffusion coefficient indicates the strong interaction between solvent molecules and crystal surfaces. For the solvent DMSO, the diffusion coefficients of FOX-7 molecules on {0 1 1}, {1 0 -1}, {1 0 1}, {0 0 1}, {1 1 -1} and {1 1 0} faces are estimated from the slope of the MSD to be $4.02 \times 10^{-9} \text{ m}^2/\text{s}$, $3.89 \times 10^{-9} \text{ m}^2/\text{s}$, $4.01 \times 10^{-9} \text{ m}^2/\text{s}$, $2.98 \times 10^{-9} \text{ m}^2/\text{s}$, $3.68 \times 10^{-9} \text{ m}^2/\text{s}$ and $3.78 \times 10^{-9} \text{ m}^2/\text{s}$, respectively. The {0 1 1} and {1 0 1} faces exhibit the largest values, indicating that the surface diffusions of solvent molecules on the two faces are faster than those of other faces. Therefore, the relative growth rates of {0 1 1} and {1 0 1} faces become slower and the morphological importance increases. On the contrary, the growth rate of {0 0 1} face

with the lowest value will improve accordingly and the corresponding face will probably disappear.

Conclusion

We predicted the crystal morphology of FOX-7 in DMSO at different temperatures using the modified attachment energy model. RDF and diffusion coefficient analysis were employed to explore the interaction energy and diffusion behaviors of solvent molecules on FOX-7 surfaces. The major results obtained in this work can be summarized as follows:

(1) The vacuum morphology of FOX-7 illustrates that the importance of main surfaces follows the sequence of $\{0\ 1\ 1\} > \{1\ 0\ -1\} > \{1\ 0\ 1\} > \{0\ 0\ 1\} > \{1\ 1\ -1\} > \{1\ 1\ 0\}$, among which $\{0\ 1\ 1\}$, $\{0\ 0\ 1\}$, $\{1\ 1\ 0\}$ and $\{1\ 1\ -1\}$ surfaces are relatively flat on the molecular level while $\{1\ 0\ -1\}$ and $\{1\ 0\ 1\}$ surfaces are uneven with many large voids.

(2) A suitable model size is proposed, of which the length, width and thickness of the supercell should be larger than $2d_c$, $2d_c$ and d_c , respectively, and the thickness of vacuum thickness and solvent amorphous cell should be larger than d_c .

(3) The morphology prediction results of the effect of DMSO and different temperatures show that the aspect ratio varies with the addition of DMSO and the changing of temperature, which demonstrates that both the solvent and temperature can influence the morphology of FOX-7.

(4) The RDF analysis shows that the solvent molecules adsorb on the FOX-7 mainly via vdW interactions and Coulomb interactions.

(5) Because of the high values of the diffusion coefficients, the growth rates of $\{0\ 1\ 1\}$ and $\{1\ 0\ 1\}$ faces are inhibited, making them the dominant growth face. Meanwhile the $\{0\ 0\ 1\}$ face with the lowest value will grow relatively fast and probably disappear.

To sum up, this study proposes a method to construct a suitable model for simulating the crystal morphology in DMSO. And it has been successfully extended to the investigation of FOX-7 grown from DMSO at different temperatures, which may

guide the explosive morphology control technology.

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