Mechanism and modelling of formation of amorphous sulfur nuclei

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The most probable shape (sphere) and size (~2.6 nm) of a critical sulfur nucleus were derived based on the random orientation of S_8 sulfur molecules during rapid nucleation.

The current interest in monodispersed colloidal spheres is caused by their applicability to the fabrication of photon crystals, computer chips and three-dimensional nanoporous materials.[1,2] The nucleation and growth of sulfur particles in solutions are also of importance because it is known[3–5] that, under specific conditions, monodisperse colloid spherulites of solution-stable[4] amorphous sulfur form in acidified aqueous solutions of thiosulfates. Elemental sulfur has many unique properties,[6–10] for example, a separate phase of amorphous sulfur particles during ageing gradually changes into α-sulfur.[3–10] In terms of mineralogy, native sulfur typically exists in a crystalline form; however, it is also found in cryptocrystalline and amorphous forms.[11–13]

The complexity of the numerical modelling of the nucleation of amorphous particles is that the real structure of an amorphous state cannot be adequately described by theoretical and experimental methods. There are different kinds of amorphous states for particular types of substances.[14–16] Their common feature is the absence of a long-range order in the structure of an object.

Earlier,[17] we proposed a method for the estimation of parameters of crystal critical nuclei based on a discrete approach. The structure of a crystal phase is assumed to be known. It is supposed that the nucleus forms on the successive addition of molecules at the positions which they would occupy in an ideal crystal. A correction is made for the length and energy of the bonds of surface molecules whose nearest neighbours are fewer than those of molecules in the bulk.

This method is used for calculating the characteristics of critical sulfur nuclei on the assumption that the growth of clusters proceeds by the addition of S_8 ring molecules.[3–6] In the rhombic crystal of α-sulfur, each S_8 molecule has two neighbour molecules at a distance of ~0.5 nm and two at ~0.6 nm.[6,18] The difference in the distances is related to different orientations of the rings. At a random orientation of S_8 rings during rapid nucleation, an averaged distance can be used in the calculated model. In this case, the long-range order is missing and an amorphous sulfur phase is formed.

At the first stage of calculation, a specific way of their addition is found from the coordinates of S_8 ring centres in a crystal.

Table 1 Parameters of a critical nucleus at layer-by-layer and random additions of S_8 molecules.

Layer-by-layer addition			Random addition		
$\Delta\mu$ (arb. units)	Number of S_8, n	A (arb. units)	$\Delta\mu$ (arb. units)	Number of S_8, n	A (arb. units)
> 0.95	2	< 1.47	0.99–0.95	7	1.02–1.30
0.95–0.61	11	1.47–5.21	0.93–0.91	16	1.56–1.88
0.60–0.55	24	5.45–6.65	0.76–0.73	27	4.75–5.56
0.54–0.50	46	6.92–8.76	0.70–0.68	53	6.57–7.63
0.49–0.38	**50**	**9.24–14.7**	**0.67–0.57**	**55**	**8.18–13.7**
0.37–0.24	119	15.4–30.9	0.45–0.37	76	22.1–28.2
≤ 0.23	≥ 148	≥ 32.3	< 0.32	> 122	> 33.8

There are two approaches to the selection of the way: (1) the addition proceeds by the coordination spheres (layer-by-layer growth), and (2) the positions of added molecules were chosen randomly, provided that the newly added molecule had at least one bond with the cluster. At the second stage of the chosen way of addition, the contribution of the cluster-infinite phase interface energy g_{sn} is calculated.[17] At the third stage, the formation energy A is calculated for various values of the relative supersaturation $\Delta\mu$ depending on the number n of molecules in a cluster: $\Delta\mu = \mu_1 - \mu_0$, where μ_1 and μ_0 are the chemical potentials of a supersaturated solution and a solution at the points of phase transition, respectively. Then, $A = -n\Delta\mu + g_{sn}$. All the energy values g_{sn}, A and $\Delta\mu$ are measured in arbitrary units.[17] The intermolecular bond energy in an infinite crystal E_∞ was taken to be unity; as a first approximation, this parameter can be estimated using the enthalpy of sulfur melting. The maximum value of $A(n)$ is used to determine the number n in the critical nucleus, and n helps us to establish the shape of a nucleus at each step of changes in the $\Delta\mu$ value.

Random addition. Ten different ways of addition were generated for approach (2). The energy of formation $A(n)$ was calculated for each of them. The results are shown in Figure 1. For simplicity, only three versions of calculations among all the possible random ways of addition are shown. All the plots

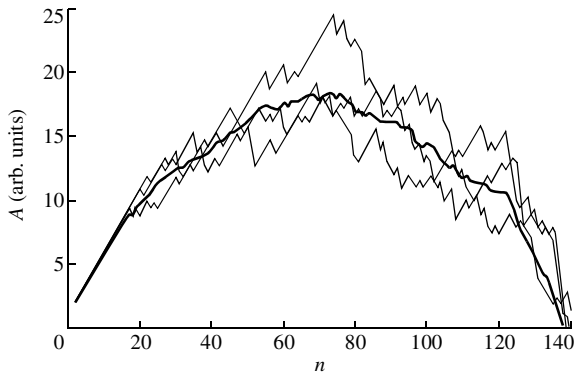

Figure 1 The energies of the formation of sulfur nuclei for different ways of the random addition of S_8 molecules for the supersaturation $\Delta\mu = 0.50$. An averaged plot is shown with a bold line.

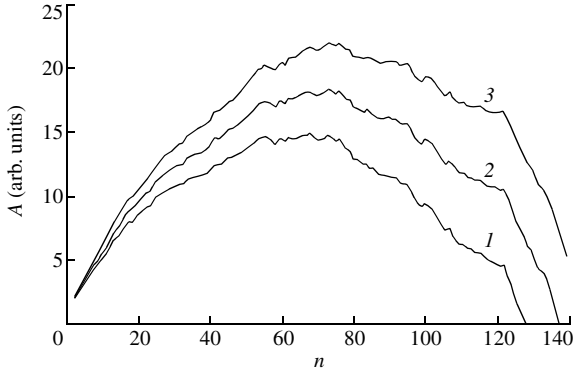

Figure 2 Averaged energy of formation of amorphous sulfur nuclei for different supersaturations: (*1*) $\Delta\mu = 0.55$; (*2*) $\Delta\mu = 0.50$; (*3*) $\Delta\mu = 0.45$. The averaging was carried out over 10 different ways for the random addition of S_8 ring molecules.

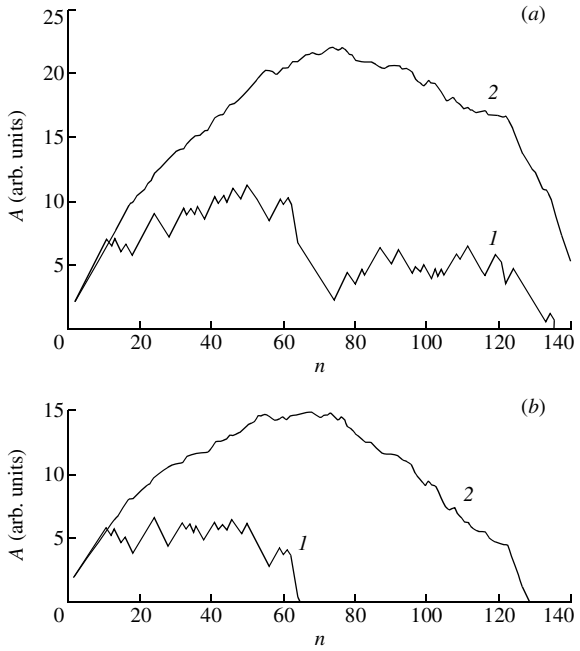

Figure 3 Energy of formation of amorphous sulfur nuclei: (*a*) $\Delta\mu = 0.45$; (*b*) $\Delta\mu = 0.55$. (*1*) layer-by-layer addition; (*2*) random addition of S_8 molecules.

relate to the same supersaturation.

Figure 2 shows the averaged plots of the energy of formation of a nucleus for three possible values of $\Delta\mu$. One can see that with the growth of $\Delta\mu = kT\ln\gamma/E_\infty$ (ref. 19) or absolute supersaturation γ [at $\gamma = 3$–5 and $T = 310$ K,[3,5] $\Delta\mu \sim 0.5$ corresponds to high γ values, if the enthalpy of sulfur melting ~12 kJ mol^{-1} (refs. 6, 10) is taken as E_∞], the values of energy barrier A and n for critical nucleus decrease. These conclusions also correspond to the classic case. A more precise calculation of the characteristics of the critical nucleus with the changes of supersaturation is shown in Table 1. The calculation was carried out with a step of 0.01 by $\Delta\mu$. A stepwise behaviour of the number of molecules in a critical nucleus is explained by the fact that even an averaged curve is nonmonotonic but has local maximums and minimums. As a consequence, the size of a critical nucleus remains constant within a range of $\Delta\mu$. Table 1 indicates that the widest supersaturation range corresponds to the size of the nucleus comprising 55 molecules of S_8.

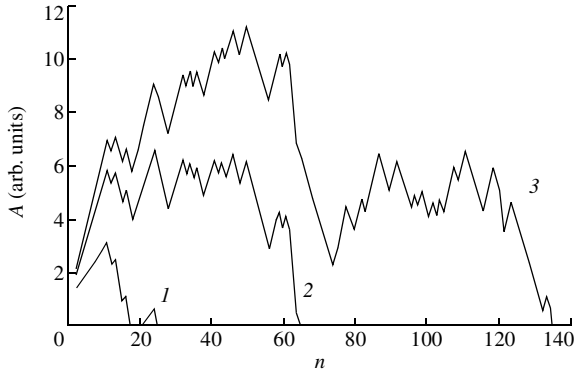

Figure 4 Energy of formation of amorphous sulfur nuclei at different supersaturations: (*1*) $\Delta\mu = 0.80$; (*2*) $\Delta\mu = 0.55$; (*3*) $\Delta\mu = 0.45$. The molecules of S_8 add to coordination spheres.

Layer-by-layer growth. It is assumed in approach (1) that the molecules fill coordination spheres in turn. The plot of the energy of cluster formation *versus* the number of S_8 molecules is shown in Figure 3 (curves *1*). For comparison, Figure 3 shows averaged plots of $A(n)$ for random addition (2) (curves *2*); (*a*) and (*b*) correspond to different $\Delta\mu$. One can see that addition to coordination spheres or a nearly spherical shape of nucleus is more profitable from the viewpoint of passing over the energy barrier during nucleation.

Figure 4 shows the plots of $A(n)$ for the addition of molecules to coordination spheres for different supersaturations. The number of energy barriers to be overcome can vary depending on supersaturation. The size of a critical nucleus remains constant within a wide supersaturation range (Table 1). The broadest range of supersaturation corresponds to the nucleus containing 50 molecules of S_8. At a lower supersaturation, a sharp increase of the size up to 119 molecules is observed.

A nucleus of amorphous sulfur containing 50 S_8 molecules is 2.6 nm in diameter.[5] The layer-by-layer addition of S_8 ring molecules is more beneficial than the random addition. The nucleus has a near-spherical shape.

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References

1 Y. Xia, B. Gates, Y. Yin and Y. Lu, *Adv. Mater.*, 2000, **12**, 693.
2 S. Auer and D. Frenkel, *Nature*, 2001, **409**, 1020.
3 E. M. Zaiser and V. K. la Mer, *J. Colloid Sci.*, 1948, **3**, 571.
4 R. Steudel, T. Göbel and G. Holdt, *Z. Naturforsch.*, 1988, **43b**, 203.
5 F. Kh. Urakaev, L. Sh. Bazarov and Yu. P. Savintsev, *J. Crystal Growth*, 1999, **205**, 223.
6 J. S. Tse, D. D. Klug, *Phys. Rev. B*, 1999, **59**, 34.
7 Chr. Biermann, R. Winter, Chr. Benmore and P. A. Egelstaff, *J. Non-Crystalline Solids*, 1998, **232**–**234**, 309.
8 K. C. Jain, M. Khetarpal, A. Gupta and N. S. Saxena, *Indian J. Pure Appl. Phys.*, 1998, **36**, 439.
9 W. Swiatkowski, *J. Non-Crystalline Solids*, 2000, **262**, 162.
10 *Elemental Sulfur. Chemistry and Physics*, ed. B. Meyer, Interscience Publ., New York, 1965.
11 N. P. Yushkin, *Mineralogiya i paragenezis samorodnoi sery v ekzogennykh mestorozhdeniyakh* (*Mineralogy and Paragenesis of Native Sulfur in Exogenetic Deposits*), Nauka, Moscow, 1968 (in Russian).
12 B. I. Srebrodol’skii, *Mineral’nye preobrazovaniya v mestorozhdeniyakh sery* (*Mineral Transformations in Deposits of Sulfur*), Naukova Dumka, Kiev, 1981 (in Russian).
13 A. A. Godovikov, *Mineralogiya* (*Mineralogy*), Nedra, Moscow, 1983, pp. 33–37 (in Russian).
14 R. Zallen, *The Physics of Amorphous Solids*, Wiley, New York, 1983.
15 S. R. Elliot, *Physics of Amorphous Materials*, Longman, London, 1983.
16 *Physics Properties of Amorphous Materials*, ed. D. Adler, Plenum Press, New York, 1985.
17 L. Sh. Bazarov, T. N. Drebushchak and F. Kh. Urakaev, *J. Crystal Growth*, 1999, **206**, 75.
18 S. C. Abrahams, *Acta Crystallogr.*, 1955, **8**, 661.
19 H. E. A. Huitema, J. P. van der Erden and H. Human, *Phys. Rev. B*, 2000, **62**, 14690.

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