

## Competition between core–shell and Janus configurations during the stratification of solutions in small volumes

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Particles with core–shell and Janus configurations are typically formed during phase transformations. The regions of existence of these particles are determined by the wetting conditions at the phase boundary and can overlap. The possibility of interconversions between core–shell and Janus configurations is modeled using a thermodynamic analysis of the Gibbs energy. The influence of the surface properties of the interphase boundary on the region of coexistence and competition between core–shell and Janus configurations is demonstrated using the Bi–Sb system as an example.

**Keywords:** phase transformations, janus particles, core–shell, thermodynamic modeling, metastable state.

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Multicomponent heterogeneous micro- and nanosized particles can have different morphologies. Of greatest practical interest are the heterogeneous core–shell structures and Janus [1,2]. Janus particles have segments with different physicochemical properties and arise quite often during synthesis [3,4] and modeling of nanoparticles [5,6].

Mutual transformations of the core–shell and Janus structures make it possible to control various properties of the material (optical, catalytic, strength, etc.). The competition between Janus and core–shell configurations is described in [1,7,8] and experimentally registered in [4]. This dynamic process is represented in the form of a diagram [1], suggesting that spinodal decomposition is the mechanism of formation of these structures. Stable and metastable core–shell structures can also arise during binodal decay [8].

The morphology is selected depending on the surface forces [5,9,10] that can be changed because of the sorption of environmental components, surface segregation of impurities included in the particle, radiation of various types [11], accumulation of electrostatic charge on the surface [12], changes in composition of coexisting phases during evaporation and extraction of the solvent [13], and also Ioffe and Reh binder effects [14].

Practical interest in the core–shell and Janus structures is associated with the production of functional materials, information display devices, and controlled drug delivery [15]. This makes the task of targeted selection or transformation of the morphology of nanoparticles relevant.

This paper outlines this phenomenon and simulates the conditions under which mutual transformations of the core–shell and Janus structures are possible.

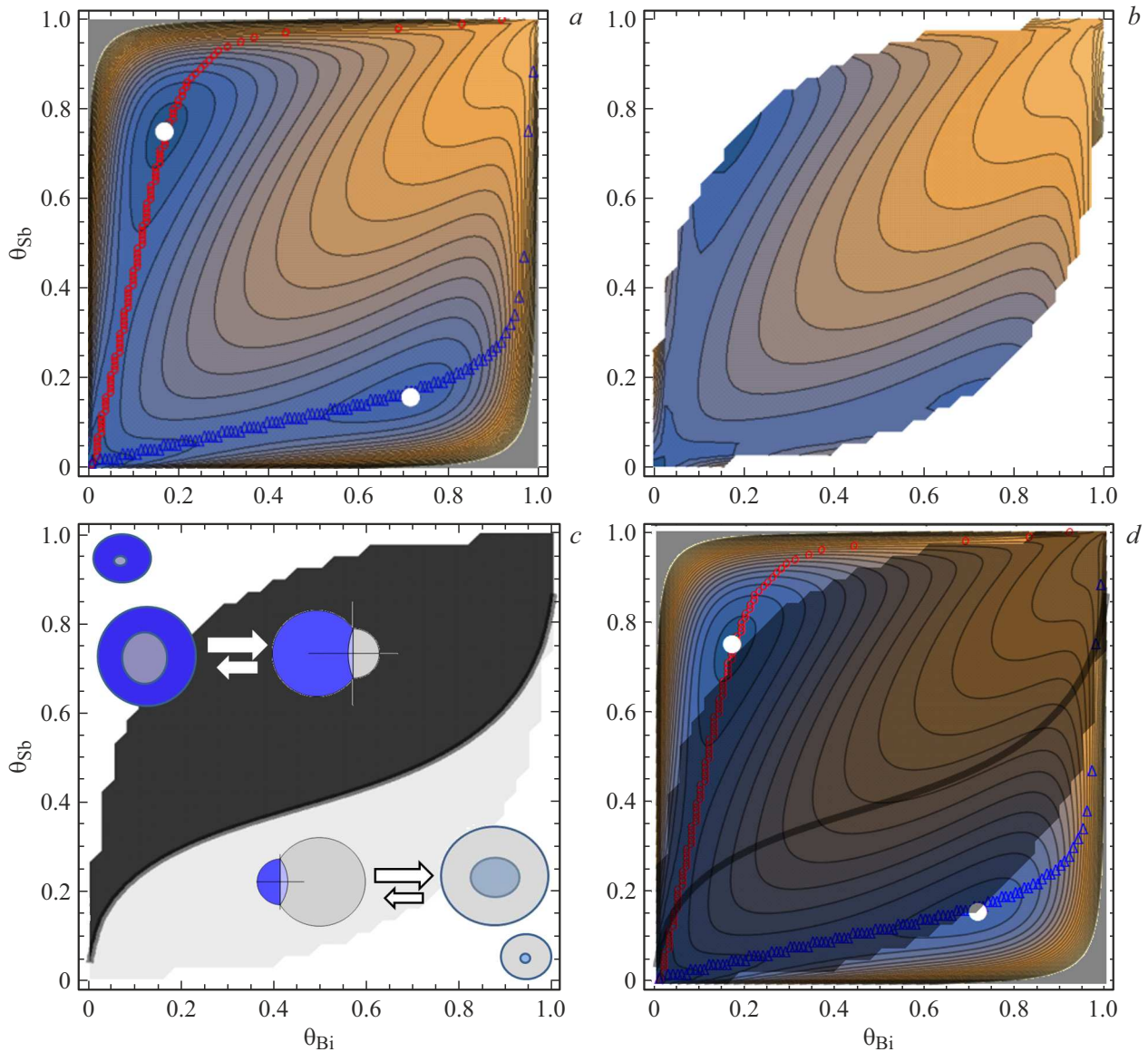
For this purpose, a thermodynamic model based on the analysis of Gibbs function was used [16]. The model describes a binary solution of sparingly soluble components,

separating into two phases. Next, we'll call  $\alpha$  phase as „initial“, and the generating  $\beta$  phase as „new“. The volume during stratification is considered constant. The stratification results in formation of a core–shell or Janus configuration.

The relationship between the particle's geometry and its physicochemical characteristics is described for Janus particles in [10], and for the core–shell structure — in [17]. The volume, composition and geometry of the phases change during the stratification process. This is accompanied by the change in the surface tension of external ( $\sigma_\alpha$ ,  $\sigma_\beta$ ) and internal ( $\sigma_{\alpha\beta}$ ) phase boundaries, which depend on  $\alpha$  and  $\beta$  phases. Janus particles occur in case of incomplete wetting when  $|\sigma_\alpha - \sigma_\beta| < \sigma_{\alpha\beta} < \sigma_\alpha + \sigma_\beta$  condition is fulfilled [10]. Outside this region, the state of core–shell or two non-interacting spheres is realized.

To evaluate the dependence of  $\sigma_\alpha$ ,  $\sigma_\beta$  on the solution concentration, empirical and semi-empirical equations [18,19] or a linear approximation  $\sigma(x) = \sigma_1 + x(\sigma_2 - \sigma_1)$  are used, where  $\sigma_1$ ,  $\sigma_2$  is the surface tension of pure components [20]. The surface tension of the phase interface  $\sigma_{\alpha\beta}$  was given as  $\sigma_{\alpha\beta} = k(\sigma_\alpha + \sigma_\beta)$ , where the parameter  $k$  allows one to vary the value of  $\sigma_{\alpha\beta}$ , taking into account factors that change the properties of interfaces (segregation of impurities and defects, special orientation or packing of molecules, etc.). In case of incoplete wetting  $|\sigma_\alpha - \sigma_\beta|/(\sigma_\alpha + \sigma_\beta) < k < 1$  both structures are considered and for lower values — only core–shell. With lower  $k$  the wetting proportion rises.

Bi–Sb system is selected for modelling [8,17], with its particles having both configurations [21]. The model is based on the calculation of the excess Gibbs function  $\Delta G(\theta_{\text{Bi}}, \theta_{\text{Sb}}) = G(\theta_{\text{Bi}}, \theta_{\text{Sb}}) - G(0, 0)$ , where  $\theta_{\text{Bi}}$ ,  $\theta_{\text{Sb}}$  are the fractions of components that have passed into the particle core,  $G(0, 0)$ ,  $G(\theta_{\text{Bi}}, \theta_{\text{Sb}})$  are the Gibbs energy of the homogeneous and heterogeneous states, including the surface energy [8].



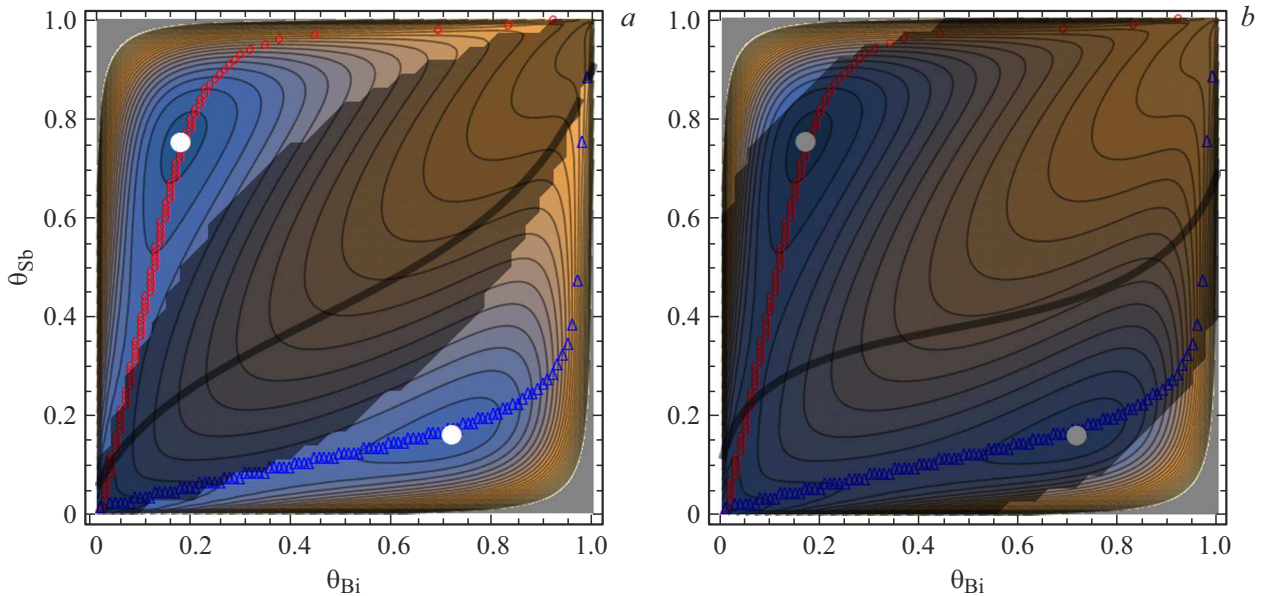
**Figure 1.** Excess Gibbs energy  $\Delta G(\theta_{Bi}, \theta_{Sb})$  of an equimolar Bi–Sb solution for micron-sized particles with the core–shell (a) and Janus (b) configurations. c — division of the region of existence of Janus particles into favorable (dark) and metastable (gray) states; d — superposition of fragments of the diagrams a, b and the equivalence line of the configuration energies.

The Janus configuration is described by three spherical segments that have a common base [10]. Each segment is characterized by volume, surface area and curvature, which depend on the ratio of surface tensions and the volume fraction of the new phase.

The modelling results are presented as a mapping of the energy surface of heterogeneous states onto a unit square [8,17]. Fig. 1 shows the energy surface of states of micron particles with the core–shell and Janus structure (at  $T = 300$  K and  $k = 0.04$ ). The point with coordinate (0, 0) corresponds to the homogenous state. The diagonal (0, 0)–(1, 1) differentiates Sb@Bi and Bi@Sb states. The designation A@B corresponds to the particles with a core from A component.

The equilibrium states Sb@Bi and Bi@Sb are denoted by light circles. They are connected to the homogeneous state by trajectories with minimal energy, on which the partial derivatives of the Gibbs energy with respect to  $\theta_i$  are equal to zero. The shading in Fig. 1, d and 2 highlights the region of existence of Janus particles, the thick line („terminator line“) separates states where the Janus configuration is thermodynamically favorable from states where it is metastable. These regions are schematically shown in Fig. 1, c.

Fig. 1 shows the case when the equilibrium states of Sb@Bi and Bi@Sb are on the boundary of the region of existence of Janus particles. The trajectories of transition to a heterogeneous state are located in this region, so it can



**Figure 2.** Change in the region of Janus configuration for micron particles of an equimolar solution of Bi–Sb with variation in the surface energy of the phase interface ( $\sigma_{\alpha\beta}$ ) with an increase in wetting ( $k = 0.03$ ) (a) and a decrease in wetting ( $k = 0.05$ ) (b).

be expected that the formation and growth of a new phase can proceed by the mechanism of heterogeneous nucleation, and in the vicinity of the equilibrium state, mutual transformations between Janus and core–shell configurations are possible.

$\sigma_{\alpha\beta}$  variation changes the probability of Janus particles formation. With the growth of wetting ( $k = 0.03$ ) Janus particles do not interfere with the equilibrium states Sb@Bi, Bi@Sb. The new phase growth trajectories are left behind the area of Janus particles existence (Fig. 2, a). With the increase of  $\sigma_{\alpha\beta}$  ( $k = 0.05$ ) the equilibrium states Sb@Bi, Bi@Sb and new phase growth trajectories exist in the region of Janus particles existence (Fig. 2, b). In this case, the core–shell and Janus structures compete, and the probability of heterogeneous nucleation of a new phase rises. Above the terminator line, the formation of Janus particles is more favorable, below it, particles with the core–shell structure are more beneficial. At higher values  $\sigma_{\alpha\beta}$  ( $k > 0.08$ ), Janus particles can exist at any composition of the new phase.

According to the given estimates, particles of a binary solution can have up to four stable/heterogeneous states. The difference in energy between the similar in composition core–shell and Janus equilibrium structures does not exceed 5%. Competition between structures occurs under good wetting ( $|\sigma_{\alpha} - \sigma_{\beta}| \approx \sigma_{\alpha\beta}$ ), Janus particles dominate under poor wetting ( $\sigma_{\alpha\beta} \approx \sigma_{\alpha} + \sigma_{\beta}$ ). In this case, the choice of morphology is determined not only by thermodynamic properties, but also by the ways of formation of the new phase, in particular by the homogeneous or heterogeneous mechanism of nucleation and the properties of critical nuclei (size, composition, formation energy), described in [8].

The morphology of micro- and nanoparticles can be controlled using factors that influence the surface properties of

phase interfaces, such as surface-active impurities, external fields, and components of external environment. No less effective factors are temperature, chemical composition of the solution and particle size [8,17].

### Conflict of interest

The author declares that he has no conflict of interest.

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