

# Equilibrium configuration of Janus particles in the case of compensated surface tension forces

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Janus particles are often formed during phase transformations in small volumes. In simulating their states, restriction to simple configurations is typically used. In this study, mechanical equilibrium stemming from compensation of surface forces has been considered. Geometric characteristics of Janus particles have been shown to significantly depend on the volume fraction of coexisting phases. Equilibrium shapes of particles are given in this paper for different volume fractions of phases at a constant surface tension on the interphase boundaries. A conclusion has been made that, in modeling Janus particles with variable segregation degree, it is necessary to take into account changes in geometric parameters.

**Keywords:** phase transformations, surface effects, mechanical equilibrium, Janus particles.

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Heterogeneous particles have quite diverse morphologies [1] which are formed with significant participation of surface energy. The Janus configuration arises under the action of surface forces and is quite often observed either in the process of synthesis [2–4] or in modeling nanoparticles by the molecular dynamics method [5,6]. In experiments, rather complex versions of this configuration are observed [2–4].

In simulation, models restricted to simple configurations are typically chosen [7–13]. The most general case is considered in [14]. This may be justified by the smallness of the surface energy contribution to the total energy of the particle. However, permissibility of such a simplification should be substantiated. For this purpose, consider the equilibrium Janus particle shape forming under the action of surface tension forces.

The Janus configuration may be represented as three spherical segments having a common base (see the Figure).

Phase  $\alpha$  fills spherical segment  $A$  with radius  $r_A$  and angle  $\varphi_A$ ; phase  $\beta$  fills spherical segments  $B$  and  $AB$  with radii  $r_B$ ,  $r_{AB}$  and angles  $\varphi_B$ ,  $\varphi_{AB}$ , respectively. Spherical segments  $A$  and  $B$  form the particle outer boundaries; segment  $AB$  represents the inner boundary. They have a common base (see the Figure), therefore, they are interrelated as follows:  $r_A \sin \varphi_A = r_B \sin \varphi_B = r_{AB} \sin \varphi_{AB}$ . Thus, radius of one of the segments and respective angles ( $r_B = r_A \sin \varphi_A / \sin \varphi_B$ ,  $r_{AB} = r_A \sin \varphi_A / \sin \varphi_{AB}$ ) are sufficient to describe the particle shape. The radius may be found from the matter conservation condition

$$V = n_1 V_1 + n_2 V_2 = V_A + V_B = V_\alpha + V_\beta,$$

$$V_f = n_{1,f} V_1 + n_{2,f} V_2 = \begin{cases} V_A - V_{AB}, & f = \alpha, \\ V_B + V_{AB}, & f = \beta, \end{cases} \quad (1)$$

where  $V_1$ ,  $V_2$ ,  $n_1$ ,  $n_2$  are the molar volumes and numbers of moles of the respective components,  $V_A$ ,  $V_B$ ,  $V_{AB}$  are the spherical segment volumes,  $V_f$  are the volumes of phases  $f = \alpha, \beta$ . Hereinafter phase  $\alpha$  is referred to as „initial“, phase  $\beta$  — as „new“. The volume is assumed to be unchanged during segregation.

Substituting into (1) the spherical segment volumes, obtain

$$\begin{aligned} V &= \frac{4}{3} \pi r_0^3 = \frac{1}{3} \pi r_A^3 \left( (1 - \cos \varphi_A)^2 (2 + \cos \varphi_A) \right. \\ &\quad \left. + \left( \frac{\sin \varphi_A}{\sin \varphi_B} \right)^3 (1 - \cos \varphi_B)^2 (2 + \cos \varphi_B) \right), \\ V_f &= \frac{1}{3} \pi r_A^3 \left( \left( \frac{\sin \varphi_A}{\sin \varphi_B} \right)^3 (1 - \cos \varphi_B)^2 (2 + \cos \varphi_B) \right. \\ &\quad \left. \pm \left( \frac{\sin \varphi_A}{\sin \varphi_{AB}} \right)^3 (1 - \cos \varphi_{AB})^2 (2 + \cos \varphi_{AB}) \right), \quad (2) \end{aligned}$$

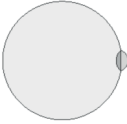
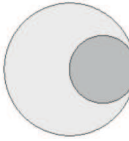
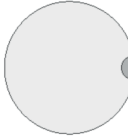
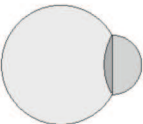
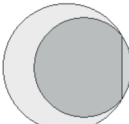
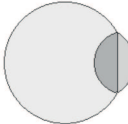
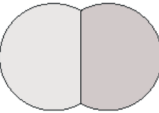
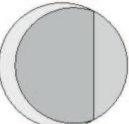
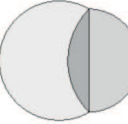
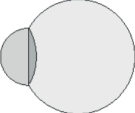
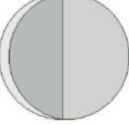
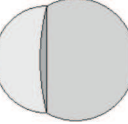
where  $r_0$  is the radius of a sphere with equivalent volume.

Equation (2) allows eliminating variable  $r_A$  and considering ratio  $r_A/r_0$  as a criterion for the particle shape deviation from a sphere. It is convenient to determine the phase volumes through segregation degree  $\theta = V_\beta/V$  that is equal to the substance volume fraction in the new phase ( $\beta$ ).

The segment volumes and shapes may change during segregation. To describe this effect, let us use an analogue of the Young's equation, which was obtained from the condition of the surface tension forces compensation at the phase interface (see the Figure):

$$\begin{aligned} \sigma_A \cos \varphi_A + \sigma_B \cos \varphi_B + \sigma_{AB} \cos \varphi_{AB} &= 0, \\ \sigma_A \sin \varphi_A + \sigma_B \sin \varphi_B + \sigma_{AB} \sin \varphi_{AB} &= 0. \end{aligned} \quad (3)$$

Spherical segment angles, segregation degree, and Janus particle shape at different ratios of surface tension

$\sigma_A = \sigma_B = \sigma_{AB}$	$\sigma_{AB} \cong  \sigma_A - \sigma_B $	$\sigma_A : \sigma_B : \sigma_{AB} = 1.5 : 2 : 1$
$\varphi = \{170, -70, 50\}$ $\theta = 0.0025$ 	$\varphi = \{170, -13, 160\}$ $\theta = 0.13$ 	$\varphi = \{170, -39, 95\}$ $\theta = 0.004$ 
$\varphi = \{150, -90, 30\}$ $\theta = 0.07$ 	$\varphi = \{150, -33, 140\}$ $\theta = 0.47$ 	$\varphi = \{150, -59, 75\}$ $\theta = 0.07$ 
$\varphi = \{120, -120, 0\}$ $\theta = 0.5$ 	$\varphi = \{120, -63, 110\}$ $\theta = 0.75$ 	$\varphi = \{120, -89, 44\}$ $\theta = 0.36$ 
$\varphi = \{90, -150, -30\}$ $\theta = 0.9$ 	$\varphi = \{90, -93, 80\}$ $\theta = 0.89$ 	$\varphi = \{90, -119, 15\}$ $\theta = 0.74$ 

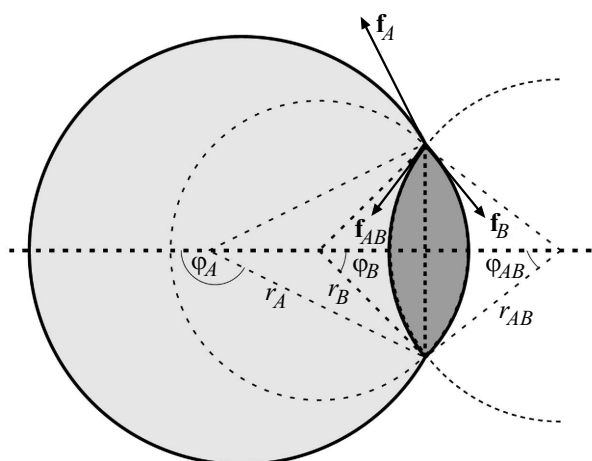
From equation set (3) it follows that

$$\sin \varphi_{AB} = -\frac{\sigma_A \sin \varphi_A + \sigma_B \sin \varphi_B}{\sigma_{AB}},$$

$$\cos(\varphi_A - \varphi_B) = \frac{\sigma_{AB}^2 - \sigma_A^2 - \sigma_B^2}{2\sigma_A \sigma_B}, \quad (4)$$

the last relation is obtained using trigonometric identities  $\cos^2 \varphi_{AB} + \sin^2 \varphi_{AB} = 1$  and  $\cos(\varphi_A - \varphi_B) = \cos \varphi_A \cos \varphi_B + \sin \varphi_A \sin \varphi_B$ . Analytical solution of set (3) is rather cumbersome and is not given here.

Thus, parameters of segments in mechanical equilibrium are interrelated by additional relations (4). Condition  $\varphi_B = \varphi_A \pm \arccos\left(\frac{\sigma_A^2 + \sigma_B^2 - \sigma_{AB}^2}{2\sigma_A \sigma_B}\right)$  is satisfied at  $|\sigma_A - \sigma_B| < \sigma_{AB} < \sigma_A + \sigma_B$  and describes the cases of a large ( $\varphi_B > \pi/2$ ) or small ( $\varphi_B < \pi/2$ ) spherical segment. Beyond the specified range, other configurations should be considered: core-shell et al. Angles of segments arranged with vertices directed to the right (see the Figure) are negative. Both outer boundaries of the Janus particle are convex; hence, solutions implying opposite signs of angles  $\varphi_A$  and  $\varphi_B$  are physically reasonable.



Janus particle crosssection and surface tension forces at the phase interface.

The Table presents individual examples of equilibrium configurations for different ratios of surface tension to segregation degree ( $\theta$ ).

Consider some special cases. States with  $\sigma_{AB} = \sigma_A = \sigma_B$  arise in the case of contact between emulsion droplets or soap bubbles. They are presented in the first column of the Table. In this case,  $\arccos\left(\frac{\sigma_A^2 + \sigma_B^2 - \sigma_{AB}^2}{2\sigma_A\sigma_B}\right) = \frac{2\pi}{3}$  and, when  $\varphi_A = \pi/6$ , a symmetrical particle with a planar phase interface ( $\varphi_B = -\varphi_A$ ,  $\varphi_{AB} = 0$ ) gets formed. Another symmetrical configuration arises when  $\sigma_{AB} = |\sigma_A - \sigma_B|$ ; the Table presents a similar case for  $\sigma_{AB} \cong |\sigma_A - \sigma_B|$ . The inclusion (phase  $\beta$ ) has a shape of a symmetrical lens at  $\varphi_B = -\varphi_{AB}$ . When  $\varphi_B = \varphi_A - \pi$ , the Janus particle shape is spherical.

Generally,  $\varphi_A \neq \varphi_B$ , and Janus particles have a non-spherical shape whose parameters change with varying new phase volume.

If the volumes of coexisting phases are expressed through segregation degree  $\theta$ , then conditions of matter conservation (2) and mechanical equilibrium (3) enable describing all the Janus configuration geometric parameters as functions of single independent variable  $\theta$ . Parameters describing the system may be assumed to be the composition ( $n_i$ ) and physical and chemical characteristics of components ( $V_i$ ,  $\sigma_f$ ).

Based on the geometric description, it is possible to estimate particle surface energy as  $w_s(\theta) = \sigma_A s_A + \sigma_B s_B + \sigma_{AB} s_{AB}$ , where  $s_k$  are the surface areas of segments  $k = A, B, AB$ . The set (3) solution corresponds to the minimum surface energy for the given  $\theta$ . This result does not account for thermodynamically equilibrium compositions of phases  $\alpha$  and  $\beta$  and for the effect of concentration on their surface tension. To accounting for the concentration and size dependences, it is necessary to analyze the total particle energy including the Gibbs energy of coexisting phases [15,16]. This complicates the search

for equilibrium configuration but allows for more adequate simulation of the specific chemical objects behavior.

Paper [16] presents thermodynamic description of a multitude of states and optimal phase trajectories of the system segregation for the core-shell configuration. Similarly, for the Janus particles there should be expected the existence of at least two paths for the system transition from the homogeneous state to heterogeneous one. The trajectory would be selected spontaneously; the choice depends on composition of the new phase nucleus which may be both the  $\alpha$  and  $\beta$  phase.

In the case of binary solutions, the core-shell particles may have two thermodynamically stable heterogeneous states [16,17]. Metastable states of the Janus particles have not yet been described. In their absence, the behavior of Janus particles and core-shell particles differs in that, when the solution is segregated, trajectories exiting the homogeneous state converge either in a single equilibrium state (Janus) or in different ones (core-shell). Mechanisms that qualitatively explain regularities of the components redistribution among coexisting phases were formulated in [17]. They allow prediction of size effects for phase diagrams. The studies allow extension of the proposed description to the case of nonspherical [18] or nonsmooth [19] surfaces.

Data presented in the Table show that the phase interface curvature strongly depends on the segregation degree. This should be taken into account in modeling nanoparticles, because restriction to only one configuration can significantly distort the results. Competition between the Janus and core-shell configurations [12,13,20] may increase the number of metastable states and nanoparticle formation pathways in the process of synthesis.

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## Conflict of interests

The author declares that he has no conflict of interests.

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