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## Metastability of Colloidal Silica Solutions at High Supersaturations

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The thermodynamic description of the breakdown of supersaturated solutions to form heterogeneous colloidal systems is quite a complex problem. In particular, it remains unclear what causes highly saturated solutions to break down to give stable colloidal disperse systems, such as sols and gels of amorphous silica, or oil-in-water microemulsions. Here, in terms of the formalism of the thermodynamics of small systems, we showed that the thermodynamic potential of highly supersaturated colloidal solutions of amorphous silica has a local minimum related closely to the condition that the number of colloidal particles in these solutions is maximum, which can be attained in a reversible isothermal process. It is this local minimum that may ensure the stability of these solutions.

Let us consider a closed supersaturated two-component system comprising  $N_s$  molecules of solvent and  $N_t$  molecules of solute at temperature  $T$  and pressure  $P$ . With regard for the low solubility of silica, we suppose that the solution is diluted ( $N_s \gg N_t$ ), and that the volume of the system  $V$  is equal to the solvent volume. Any solution can be regarded [1] as a microheterogeneous colloidal system. Let us examine the case when the initial supersaturation of the solution is above the critical one, such that the rate of formation of primary particles of the critical radius is high, and their abundant production is not a limiting step for the processes in this disperse system. In terms of the thermodynamics of small systems [2, 3], the Gibbs potential of the disperse system, and its change in a process at constant  $P$ ,  $T$ , and  $N_s$  are respectively written as [3]

$$G = N_s \mu_{ss} + N \mu' + N_p \mu_p, \quad (1)$$

$$dG = \mu' dN + \mu_p dN_p + \mu N_p d\bar{n}, \quad (2)$$

where  $N \leq N_t$  is the number of molecules in the solution,  $N_p$  is the total number of colloidal particles, and  $\bar{n}$  is the

average number of molecules in them. The chemical potential  $\mu_p$  of noninteracting particles has the form [3]

$$\mu_p(P, T, X_p, \bar{n}) = kT \ln X_p + \psi_p(P, T, \bar{n}),$$

where  $X_p = N_p/N_s \ll 1$ . The chemical potentials of solute and solvent molecules are respectively expressed as  $\mu'(P, T, X) = kT \ln x + \mu_0(P, T)$  and  $\mu_{ss}(P, T, X, X_p) = \mu_{s0}(P, T) - kT(X + X_p)$ , where  $X = N/N_s \ll 1$ ;  $x = X/X_0$  is the solution supersaturation;  $X_0 = N_0/N_s$  is the concentration of solute molecules in the supersaturated solution;  $\mu_0$  is their chemical potential, which is equal to that in the disperse phase; and  $\mu_{s0}$  is the chemical potential of pure solvent. Equation (2) also contains the chemical potential  $\mu$  of molecules in the disperse phase [3]:

$$\mu(P, T, \bar{n}) = \left( \frac{\partial \mu_p}{\partial \bar{n}} \right)_{N_p, P, T} = \left( \frac{\partial \psi_p}{\partial \bar{n}} \right)_{P, T}. \quad (3)$$

Since the number of molecules in a closed system is conserved,

$$\bar{n} N_p + N = N_t, \quad (4)$$

then,

$$dG = (\mu_p - \bar{n} \mu') dN_p + (\mu - \mu') N_p d\bar{n}. \quad (5)$$

As one can see from Eq. (5), the condition of thermodynamic equilibrium ( $dG = 0$ ) is reduced to the conditions of phase equilibrium, which are given by the equalities  $\mu' = \mu$  and  $\mu_p = \bar{n} \mu'$ . The latter equality is analogous to the conditions of association equilibrium [1, 4] in ensembles of molecular associates noninteracting with one another; these conditions determine the function  $P_n$  of distribution of ensembles with respect to the number of their constituting particles in unsaturated (or slightly saturated) systems.

Since the function  $\mu_p(X_p, \bar{n})$  is generally unknown, let us make an approximate analysis of the process of change in the Gibbs potential  $G(N_p, \bar{n})$  of the disperse system. The function  $P_n$  of distribution of particles with respect to the number of molecules they are composed of is unknown and, moreover, varies in the course of the process. Let us assume that this distribution is represented by a sufficiently narrow peak with a top at  $n = \bar{n}$ . In this approximation, neglecting the entropy contribu-

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tion related to the scatter of particles in the number of their constituting molecules, and supposing that each of the particles consists of  $n = \bar{n}$  molecules, we represent  $\mu_p$  by the expression that has been obtained [2] for an incompressible substance in a monodisperse system (the  $N, P, T$ -model). Let us assume that particles have the shape of spheres of radius  $R$ , and express their surface energy in an approximation valid at  $n \gg 1$  as  $U = 4\pi R^2\alpha = \alpha sn^{2/3}$ , where  $\alpha$  is the surface tension, which is independent of  $R$ ;  $s = 4\pi r^2$ ;  $r$  is the radius of a molecule, which obeys the relation  $R^3 = r^3n$ . Then we have [2]

$$\mu_p(\bar{n}) \cong -kT \ln \frac{aV(kT)^3 \bar{n}^4}{N_p} + \alpha s \bar{n}^{2/3} + \bar{n}\mu_0, \quad (6)$$

$$\mu(\bar{n}) \cong \mu_0 + \frac{bkT}{\bar{n}^{1/3}} - \frac{4kT}{\bar{n}}, \quad b = \frac{2\alpha s}{3kT}, \quad (7)$$

where  $a = (0.4)^{3/2} 64\pi^5 (mr)^3 / h^6$ ,  $h$  is Planck's constant, and  $m$  is the weight of a molecule.

Note that the above approximation cannot be good for describing the transition of slightly saturated systems into the metastable state, since it presupposes that the function  $P_n$  has a maximum. However, in our case, this function in the final state has no maximum; conversely, it has a minimum at the critical particle radius [1, 5]. Let us treat this question using the example of an aqueous solution of silica. Taking the silica particle density to be  $2400 \text{ kg/m}^3$ , and the silica solubility to be  $0.2 \text{ kg/m}^3$  [6], at  $T = 300 \text{ K}$ , we have that  $r = 2.14 \times 10^{-10} \text{ m}$ ,  $N_0/V = 2 \times 10^{24} \text{ m}^{-3}$ , and  $a(kT)^3 V/N_0 = 2 \times 10^{13}$ . At  $\alpha \approx 46 \text{ mJ/m}^2$  [6], we obtain that  $b \approx 4$ . Note that this  $b$  corresponds to a critical supersaturation of  $x_c \approx 3$  [1, 7]. Computer analysis showed that the function  $G(N_p, \bar{n})$  calculated by Eqs. (1), (4), and (6) at  $b = 4$  for low initial supersaturations  $x_i = N_i/N_0$  at  $N_p > 0$  has no singularities. A singularity corresponding to the condition  $dG = 0$  emerges only when the supersaturation  $x_i$  exceeds 2.05, i.e., is on the order of the critical supersaturation. Although the analysis revealed that the function  $G(N_p, \bar{n})$  has a singularity, this singular point proved not to be an extremum but a saddle point. It cannot be a point of stable equilibrium; however, at this point,  $\mu_p = n\mu'$ , and therefore, near this point, there should be a region where  $\mu_p - n\mu' < 0$ , i.e.; a region where the particle formation is thermodynamically advantageous, and where a point of stable equilibrium may hence occur.

Let us examine the change in the Gibbs potential of the disperse system in a reversible process under the condition that  $\mu' = \mu$ . In such a process, the system must necessarily pass through the saddle point (since, at this point,  $\mu' = \mu$ ); but in doing so, as Eq. (7) shows, the

Thomson (Kelvin) equation should be obeyed all the time:

$$\ln x = \ln \frac{X}{X_0} \cong \frac{b}{\bar{n}^{1/3}} - \frac{4}{\bar{n}}; \quad (8)$$

i.e., the particle radius is maintained equal to the critical radius. The last term in Eq. (8) is the correction for the rotational and translational Brownian motions of particles, and for their total entropy. At  $b = 4$  for  $\bar{n} > 10$ , this correction is comparatively small. If condition (8) is met, then, along with equality (4), one more relationship emerges among the variables  $N, N_p$ , and  $\bar{n}$ , and only one of these variables remains independent. If  $\bar{n}$  is chosen as an independent variable, then Eq. (5) at  $\mu' = \mu$  takes the form

$$dG(\bar{n}) = (\mu_p - \bar{n}\mu') \frac{dN_p}{d\bar{n}} d\bar{n}. \quad (9)$$

The function  $G(\bar{n})$  has extrema at the points where one of the factors on the right side of Eq. (9) becomes zero. Thus, its minimum can be determined by either the condition of association equilibrium or the existence of extremum of the function  $N_p(\bar{n})$ . To reveal what determines the minimum at high supersaturations, let us study the function  $G(\bar{n})$  graphically.

Substitution of Eqs. (4) and (6) and the expressions for  $\mu'$  and  $\mu_s$  into Eq. (1) yield the difference  $G(\bar{n})$  (divided by  $kT$ ) of the function  $G(\bar{n})$  and the Gibbs potential  $G_0 = N_s(\mu_{s0} - kTX_0) + N_t\mu_0$  of the system in its final state when the solution has ceased to be supersaturated:

$$\frac{\Delta G(\bar{n})}{kT} = \frac{G(\bar{n}) - G_0}{kT} = \frac{N_t}{x_i} \left[ \frac{x_i - x(\bar{n})}{\bar{n}} \left( \frac{3b\bar{n}^{-2/3}}{2} - \ln \frac{eVa(kT)^3 \bar{n}^5}{N_0(x_i - x(\bar{n}))} \right) + x(\bar{n})(\ln x(\bar{n}) - 1) + 1 \right],$$

where  $x(\bar{n})$  is given by expression (8).

The figure presents the plots of  $\Delta G(\bar{n})$  versus  $\bar{n}$  at high initial supersaturations  $x_i > x_c$ . Two close values of  $x_i$  are taken. The figure also shows the curves of the number  $N_p$  of particles in the system as calculated by Eqs. (4) and (8). The calculations were performed for a sufficiently small subsystem containing  $N_t = 10000$  solute molecules. With increasing  $\bar{n}$ , each of the functions  $\Delta G(\bar{n})$  at  $N_p(\bar{n}) > 0$  passes through one minimum (at  $\bar{n} = \bar{n}_{\min}$ ) and one maximum (at  $\bar{n} = \bar{n}_{\max}$ ), and further monotonically decreases. The figure demonstrates that the minima of the functions  $\Delta G(\bar{n})$  coincide with the extrema of the functions  $N_p(\bar{n})$  (and, hence, their maxima correspond to the condition of association equilibrium, i.e., to the saddle point). Note that, at  $\bar{n} < \bar{n}_{\max}$ ,

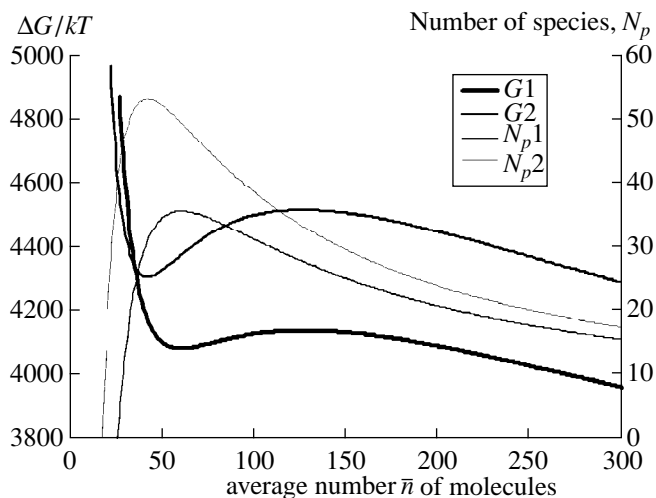
$\Delta G(\bar{n})$  decreases when  $N_p(\bar{n})$  increases, and vice versa. As one can see from Eq. (9), this corresponds to the inequality  $\mu_p - n\mu < 0$ ; i.e., the process takes place in the region where the formation of particles of the critical radius is thermodynamically advantageous (which is due to their Brownian motion taken into account by the first, negative term of Eq. (6)).

Let us consider a point  $A$  at  $\bar{n} = n_A < \bar{n}_{\min}$  in the curve  $\Delta G(\bar{n})$ . At this point, the number of particles in the system is  $N_p = N_p(n_A)$ . Since the function  $N_p(\bar{n})$  has a maximum at  $\bar{n} = \bar{n}_{\min}$ , then, in the curve  $\Delta G(\bar{n})$ , one can always find a point  $B$  (at  $\bar{n} = n_B$ ) at which the number  $N_p = N_p(n_B)$  of particles in the system is the same. The point  $\bar{n} = \bar{n}_{\min}$  separates the curve  $G(\bar{n})$  into two branches ( $A$  and  $B$ ). The  $n_A$  and  $n_B$  values at a given  $N_p$  are the roots of the equation  $\mu'(\bar{n}) = \mu(\bar{n})$  (Eq. (8)), which correspond to the two branches of the curve  $\Delta G(\bar{n})$ . Let us examine the transition of the system from point  $A$  to point  $B$ , which occurs with the proviso that  $N_p(\bar{n}) = N_p = \text{const}$ . As Eq. (5) shows, independently of the approximations we made, the change  $\Delta G_{AB}$  in the Gibbs potential of the disperse system in this transition is found from the expression

$$\Delta g_{AB} = \frac{\Delta G_{AB}}{N_p} = \int_{n_A}^{n_B} (\mu(\bar{n}) - \mu'(\bar{n})) d\bar{n}, \quad (10)$$

where  $\Delta g_{AB}$  is the change in the Gibbs potential per one small system of the volume  $V/N_p$ , which consists of a particle and its surrounding solution.

As one can see from Eq. (10),  $\Delta G_{AB}$  is related only to the molecular transfer processes, which are the same within each of the small systems. Hence, although the small systems are open, Eq. (10) at  $N_p = \text{const}$  is identical to the analogous equation for a separate closed small system with a given  $N_i/N_p$ . Analysis of equations similar to Eqs. (8) and (10) by the example of the formation of a single drop in a closed system has demonstrated [8] that the larger root of Eq. (8) corresponds to a state of stable phase equilibrium between the vapor and the particle of a large (in comparison with the Volmer nuclei) critical size. Consequently, during its growth in the closed system, the drop of the new phase initially passes through a state of unstable equilibrium and then arrives at a state of stable equilibrium, in which the thermodynamic potential of the system is minimal [8]. In our case, this implies that the disperse system at constant  $N_p$  should pass into the state of stable phase equilibrium such that  $\mu'(n_B) = \mu(n_B)$ , in which their constituting small systems are also in stable equilibrium, and which corresponds to the point  $\bar{n} = n_B(N_p)$  in the branch  $B$  of the curve  $G(\bar{n})$  at which (at a given  $N_p$ ) the Gibbs potential of the system is minimum.



Changes  $(G - G_0)/kT$  in the Gibbs potential of a closed small water-silica subsystem ( $N_i = 10000$ ) and numbers  $N_p$  of its constituting particles as functions of the average number  $\bar{n}$  of molecules in a particle at  $b = 4$  and  $x_i = 3.3$  (curves  $G1$  and  $N_{p1}$ ) and  $3.7$  (curves  $G2$  and  $N_{p2}$ ).

Since the function  $G(\bar{n})$  was calculated above in the approximation that the distribution function is narrow, then the minimum value of the Gibbs potential only approximately agrees with the branch  $B$  we calculated. Therefore, the applicability of the approximation made should be discussed. At  $n = n_B$ , a particle in a closed system is absolutely stable only with respect to its growth [8]. With respect to the reverse process, i.e., its dissolution, its stability is relative, since the activation energy  $\Delta g_{BA} = -\Delta g_{AB} > 0$  of this process is finite. This activation energy is the difference  $\Delta W$  between the work done in formation of unstable nuclei and that done in formation of stable particles [8]. The notion of the work  $W$  done in formation of a particle of a new phase plays an important role in the theory of phase transitions, since knowledge of  $W$  enables one to judge the statistical distribution of nuclei produced by fluctuations with respect to the number of their constituting molecules:  $P_n = A(W)\exp(-W/kT)$ , where  $A(W)$  is a slowly varying function of  $W$  [5, 8]. As one can see from here, the function  $P_n$  for the ensemble of small systems (if their number  $N_p$  is constant or varies slowly enough with time) should have a maximum at  $n = n_B(N_p)$ . At  $\Delta g_{BA} \gg kT$ , this distribution should be narrow enough, since the ratio between the populations of the states  $n = n_A$  and  $n = n_B$  is approximately equal to  $\exp(-\Delta g_{BA}/kT) \ll 1$ , and the populations of states with  $n > n_B$  abruptly decreases with increasing  $n$  (because  $W$  rises [8]). Hence, small systems in this ensemble should be mainly in the state  $n = n_B$ , experiencing only small deviations  $\delta n \ll n_B - n_A$  from this point.  $\Delta g_{BA}$  should be larger, the longer the interval  $[n_B - n_A]$  of integration is in Eq. (10). Therefore, the narrow distribution

approximation is better, the farther the point  $n_B(N_p)$  is from the initial point  $\bar{n} = \bar{n}_{\min}$  of the branch  $B$  of the curve  $G(\bar{n})$ . At the same time, this approximation is obviously invalid in the branch  $A$ , since, at  $n = n_A$ , the small systems are unstable.

Since the disperse system is an ensemble of open small systems, then their number  $N_p$  can also vary after this system has attained the state of stable phase equilibrium  $\mu' = \mu$  at the point  $\bar{n} = n_B(N_p)$  in the branch  $B$  of the curve  $G(\bar{n})$ . But further decrease in the Gibbs potential with varying  $N_p$  should proceed along this branch, since it is in this branch that the Gibbs potential is minimum at each current value of  $N_p$ . Of greatest interest is the case when, as a consequence of a spontaneous process, the disperse system has arrived at a point of the branch  $B$  where  $\bar{n} = n_B < \bar{n}_{\max}$ . In this case (figure), further decrease in the Gibbs potential of the disperse system is accompanied by a rise in the number of particles and a diminution in the average number of their constituting molecules until  $\bar{n} = \bar{n}_{\min}$ . In this process, the disperse system is stable with respect to the particle growth. On the one hand, its stability is due to the fact that separate small systems in the branch  $B$  under the assumption of their closeness are absolutely stable with respect to the particle growth; and on the other hand, the stability of the dispersed system is caused by the fact that, as the figure shows, increase in  $\bar{n}$  in the ensemble of open small systems brings about rise in the Gibbs potential of the disperse system as a whole, which requires work to be done by an external source. In this case, the minimum work to be done for the system to negotiate the saddle point at  $\bar{n} = \bar{n}_{\max}$  (which is equal to the change in the thermodynamic potential of the disperse system in the reversible process) is large enough. For example, as one can see from the figure, the increase in the Gibbs potential in such a process at  $x_i = 3.7$  in the transition from the point  $\bar{n} = \bar{n}_{\min} = 42$  (at which the diameter of silica particles in

the suspension is  $d = 2r\bar{n}^{1/3} = 1.5$  nm) to the point  $\bar{n} = \bar{n}_{\max}$  for even a very small subsystem (containing as few as 50 colloidal particles) of the disperse system is  $209$  kT.

Thus, our considerations have demonstrated that the microheterogeneous system of amorphous silica particles of proper dispersity at sufficiently high concentration can be stable enough with respect to the increase in the average particle size because of fluctuations of its energy already at the level of its smallest subsystems, each containing about ten colloidal particles. Note that the obtained particle diameter  $d = 1.5$  nm is quite characteristic of amorphous silica gels [6].

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