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On the Phase Approach in the Thermodynamics of Aggregative Systems

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The conditions of phase equilibrium for particles of an aggregative polydisperse system are considered. It is shown that only stationary points in the equilibrium distribution curve satisfy simultaneously the conditions of aggregative equilibrium and phase equilibrium. At other points, the curve shape determines the change of the chemical potential corresponding to the phase equilibrium.

Two types of polydisperse aggregative systems are the most widely known: the population of nuclei of a new phase in the process of phase transition and associated solutions including micellar ones. The analysis of the equilibrium distribution of particles in an aggregative system plays a key role in the thermodynamics and kinetics of phase transitions and micellization. The analysis is based on the aggregative equilibrium condition:

$$\mu_n = n\mu \tag{1}$$

where μ_n is the chemical potential of an aggregate consisting of n molecules, μ is the chemical potential of the monomeric form of matter and n is the aggregation number. The equilibrium distribution itself is derived from equation (1),[1] as well as the mass action law used especially when considering micellization in surfactant solutions.[2] The approach based on the mass action law is often opposed to the phase approach where every particle of aggregative system is treated as a region of a certain phase α surrounded by a phase β, *i.e.* a polydisperse system is considered as a heterogeneous one. Herewith, the ordinary phase equilibrium condition is used:

$$\mu^\alpha = \mu^\beta \tag{2}$$

In reality, the aggregative equilibrium and phase equilibrium are independent to a certain extent. These are not alternative approaches to the description of something the same, but different phenomena which may be combined or, the reverse, realized separately. The delicate problem of the relation between the aggregative equilibrium and phase equilibrium was touched upon earlier,[3,4] but mainly only extreme points in the equilibrium distribution curve were analysed. This presentation considers the whole run of the distribution curve from the phase equilibrium standpoint.

Statistical mechanics gives the following expression for the chemical potential:[1]

$$\mu_n = G_n^0 + kT\ln({}_n^3 c_n f_n) \tag{3}$$

where G_n^0 is the Gibbs energy for a separately taken aggregate of n molecules with resting centre of mass in a pure solvent (in the absence of other aggregates), k is the Boltzmann constant, T is temperature, ${}_n = h(2\pi m_n kT)^{1/2}$ is the mean de Broglie wavelength for a given aggregate (h is the Planck constant, m_n is the aggregate mass) and c_n and f_n are its concentration and activity coefficient, respectively. The quantity ${}_n^{-3}$ is the partition function for the aggregate translational motion. Correspondingly, $kT\ln{}_n^3$ is the contribution to free energy from the translational motion. Similarly, $kT\ \ln f$ represents the contribution from the interaction between aggregates including monomers. Uniting $kT\ln({}_n^3 f_n)$ and G_n^0, we write equation (3) as:

$$\mu_n = G_n + kT\ln c_n \tag{4}$$

where G_n is the Gibbs energy already related to a moving and interacting aggregate.

Following the usual formalism of the thermodynamics of a small spherical particle,[5] we may write:

$$G_n = \sigma A/3 + \mu^\alpha n \tag{5}$$

where σ is the surface tension of an aggregate, A is its surface area (to be more exact, the area of the surface of tension) and μ^α is the chemical potential of the molecules in the internal phase α of the aggregate. We emphasize that all the quantities in equation (5) refer to a real moving and interacting aggregate (a similar expression may be written for an aggregate with resting centre of mass:[5] it will be of the same form but with different values of the quantities). The Gibbs–Duhem equation for a spherical and equilibrium (inside it) disperse particle will also be needed:[6]

$$\mathrm{d}(\sigma A/3) + n\mathrm{d}\mu^\alpha = 0 \tag{6}$$

Now, differentiating equation (4) with respect to n with equations (5) and (6) in mind, we obtain:

$$\mathrm{d}\mu_n/\mathrm{d}n = \mu^\alpha + kT\mathrm{d}\ln c_n/\mathrm{d}n \tag{7}$$

On the other hand, differentiating equation (1) along the distribution curve (*i.e.* at constant μ), we find:

$$\mathrm{d}\mu_n/\mathrm{d}n = \mu = \mu^\beta \tag{8}$$

where the self-evident condition $\mu = \mu^\beta$ has been used since the monomers are situated automatically in outer phase β. Comparing equations (7) and (8), we arrive at a remarkable relationship:

$$\mu^\alpha + kT\mathrm{d}\ln c_n/\mathrm{d}n = \mu^\beta \tag{9}$$

which shows that the condition of phase equilibrium (2) is realized only at those points in the equilibrium distribution curve where the condition $d \ln c_n/dn = 0$ is satisfied. These may be extreme points for concentration or inflection points in the $c_n(n)$ curve with a horizontal tangent. A maximum of c_n, for example, corresponds to micelles. A minimum of c_n corresponds to equilibrium Gibbs–Volmer nuclei in the population of nuclei of a new phase. An inflection point corresponds to the boundary state, for example, to the critical micelle concentration.[7]

Since $\mu^\beta = \mu$, this quantity remains constant on moving along the distribution curve at a given physical state of a system. Then, differentiating equation (9) along the distribution curve, we obtain the condition:

$$d\mu^\alpha/dn = -kTd^2 \ln c_n/dn^2 \tag{10}$$

from which it is seen that the shape of the distribution curve determines completely the change of chemical potential μ^α at each point of the curve. If the curve is plotted as $\ln c_n$ *vs.* n, then μ^α increases at convex parts and decreases at concave parts of the curve with increasing aggregation number n. Inflection points correspond to extremes of chemical potential. If the curve is plotted as c_n *vs.* n, then μ^α increases by necessity with n at convex parts of the curve: the transition from increasing to decreasing can occur only at a concave part.

Thus, we arrive at the following conclusion. The conditions of aggregative equilibrium and phase equilibrium are realized simultaneously only at stationary points in the equilibrium size distribution curve for particles in a polydisperse aggregative system. Only the aggregative equilibrium condition holds at all other points, and the change of the chemical potential corresponding to phase equilibrium is completely determined by the shape of the distribution curve.

References

1 F. M. Kuni and A. I. Rusanov, *Teor. Mat. Fiz.*, 1970, **2**, 265 (in Russian).

2 A. I. Rusanov, *Mitselloobrazovanie v rastvorakh poverchnostno-aktivnykh veshchestv (Micellization in Surfactant Solutions),* Khimiya, St. Petersburg, 1992 (in Russian).

3 A. I. Rusanov, *Kolloidn. Zh.*, 1987, **49**, 932 [*Colloid J. USSR (Engl. Transl.)*, 1987, **49**, 816].

4 A. I. Rusanov, *Adv. Colloid Interface Sci.*, 1992, **38,** 271.

5 A. I. Rusanov, *Phasengleichgewichte und Grenzflachen-erscheinungen,* Akademie-Verlag, Berlin, 1978 (in German).

6 A. I. Rusanov, *Kolloidn. Zh.*, 1981, **43**, 890 [*Colloid J. USSR (Engl. Transl.)*, 1981, **43**, 723].

7 E. Ruckenstein and R. Nagarajan, *J. Phys. Chem.*, 1975, **79**, 2622.

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