Interface Tension in Binary Systems with Curved Boundaries (Including the Sphere of a Nanosize)

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Abstract. Within the framework of finite thick method the equation of the interfacial tension isotherm for a disperse particle of radius \( r \) (including the sphere of nanosize) immersed in a dispersive medium is obtained with taking into account the particle interactions in binary system. The account of particle interactions in condensed phases far from a critical condition has been conducted with use of a rigid transition layer model when the value of molar partial surface does not vary with change of an interfacial tension. Cases when the pressure in the dispersive medium and a dispersive particle are independent on temperature are considered. The known formulas received earlier by other authors follow from obtained equation of the interfacial tension isotherm at corresponding assumptions, including expressions for one-component system, flat boundary between two solutions in a binary system, condensed phase at the boundary of vapor and others.

1. Introduction
In our days it is interesting to study the systems containing a disperse phase in nanometer range. Interest to such objects is connected both with the further development of fundamental science and with their special properties (shift of energy states due to dimensional quantization, change of electron-hole processes and many others). With development of nanotechnology and nanoelectronics there is a need for concrete and reliable data on properties of small particles and thin films. In particular the results of researches in this area should lead to development of scientific bases of nanotechnology and allow one to create purposefully the objects with the preset size, structure and properties.

The equation of the interfacial tension isotherm in the binary system consisting of a disperse particle with curvature radius \( r \) (phase \( \alpha \)) and a dispersive medium (phase \( \beta \)) has been obtained in [1]. It is derived within the framework of the known thermodynamic finite thick method (the method of Vander-Vaals-Huhengeim-Rusanov) [2]. This equation is exact and has strict thermodynamic character for systems, where chemical potentials of components in all bulk phases and in a transitive layer between them (phase \( \sigma \)) are proportional to corresponding logs of concentrations (\( \mu_i \sim \ln x_i \)).

It is of interest to obtain the similar equation of the interfacial tension isotherm for the real and concentrated systems with regard for particle interactions. The thermodynamic activities \( a_i \) (or coefficients of activity \( f_i \)) of components \([2, 3]\) have been involved in thermodynamic theories of phase equilibriums and surface phenomena of the systems for which it is possible to expand the big statistical sum of a solution \([4, 5]\).
2. Basic results and their discussion

Let us start from the condition of minimization of the thermodynamic potential of a heterogeneous system. As a dividing surface we shall choose a Gibbs tension surface. At such choice of a dividing surface the interfacial tension will be equal to the work of formation of the surface unit [2]. The pressures in phases $p^{(a)}$ and $p^{(b)}$ for this position of a dividing surface are connected by the relation

$$\frac{dp^{(a)}}{dr} = \frac{2}{r} \frac{d\sigma}{dr} - \frac{2\sigma}{r^2},$$

where $\sigma$ is the interfacial tension. From the joint solution of two equations coming from the equilibrium conditions of $\alpha$ phase with interface layer ($\sigma$) and the second bulk phase ($\beta$), we obtain [1]

$$\omega_i d\sigma + \left( \frac{v_i^{(\sigma)} - v_i^{(a)}}{v_i^{(b)} - v_i^{(a)}} \right) \left( \frac{2\sigma}{r} \right) = \frac{v_i^{(\sigma)} - v_i^{(a)}}{v_i^{(b)} - v_i^{(a)}} \sum_{j} g_{ij}^{(\sigma)} \frac{dx}{dx}^{(\sigma)}$$

$$+ \frac{v_i^{(b)} - v_i^{(\sigma)}}{v_i^{(b)} - v_i^{(a)}} \sum_{j} g_{ij}^{(a)} \frac{dx}{dx}^{(a)} - \frac{v_i^{(\sigma)} - v_i^{(a)}}{v_i^{(b)} - v_i^{(a)}} \sum_{j} g_{ij}^{(b)} \frac{dx}{dx}^{(b)}$$

where $i$ and $j$ take values 1 and 2 ($i \neq j$), $g_{ij}$ is the second derivative of molecular thermodynamic potential $g$ over the concentration of $j$-th component, $v_i^{(\sigma)}$ is a part of average partial molar volume of the interface layer $v_i^{(\sigma)}$, located next to the part of bulk phase $\beta$ (the dispersive medium), top subscripts indicate phase, bottom - components.

Partial derivatives $g_{ij}$ in two-component bulk phases $\alpha$ and $\beta$ are taken at the constant temperature $T$ and correspondingly pressures $p^{(a)}$ and $p^{(b)}$, and for an interface layer- at the constant $T$, $\sigma$, $p^{(a)}$ and $p^{(b)}$. Let us use the Gibbs-Dugem equation, which is the condition equation for any phase of considered system including an interfacial layer, under conditions of constancy of the quantities, indicated above. In this case relation (2) yields

$$\omega_i d\sigma + \left( \frac{v_i^{(\sigma)} - v_i^{(a)}}{v_i^{(b)} - v_i^{(a)}} \right) \left( \frac{2\sigma}{r} \right) = RT \left( \frac{d\omega_i^{(\sigma)}}{v_i^{(\sigma)}} - \frac{d\omega_i^{(b)}}{v_i^{(b)}} \right)$$

$$- \frac{d\omega_i^{(a)}}{v_i^{(a)}}$$

Last relation has strict thermodynamic character and it is received without any assumptions. Its integration, however, is possible within the framework of certain models for a transition layer and bulk phases of systems.

The model of a rigid surface layer which can be quite good approximation for condensed phases far from a critical condition is used successfully in thermodynamics of the surface phenomena [2]. The well known equation of the surface tension isotherm at the boundary of vapor for binary system (Butler's equation [6]), found wide application in practice, is derived within the framework of this model [6]. The similar equation for the description of dependence of the interfacial tension at the boundary of two solutions on structure of bulk phases and a transition layer between them in isothermal conditions is received in [7] with use the rigid model approximation. Within the framework of this model it is possible to consider a number of the major characteristics for the interface boundaries of nanoparticles (work of adhesion, wetting contact angles, spreading coefficient) in binary systems [8,9,10]. Due to the infinitely large value of the conditional module of elasticity in surface layer ($E=\infty$) in this approximation the value of partial molar surface $\omega_i$ will not vary with change of the tension $\sigma$. The partial molar surfaces and partial molar volumes in all phases of heterogeneous system in this case coincide with similar values for components ($\omega_i \approx \omega_{hi}$, $v_i^{(a)} \approx v_{hi}^{(a)}$, $\xi=\alpha,\beta,\sigma$). Let us integrate the equation (3) under these conditions taking out the quantities $\omega_{hi}$ and
\[ \frac{v_i^{(\sigma)}}{v_i^{(\beta)}} - \frac{v_i^{(\alpha)}}{v_i^{(\beta)}} \] from the integral in the right hand side and change of curvature radius from infinity (flat boundary) up to the current value \( r \). Of (3)

\[ \sigma = \sigma_{0i} + \frac{RT}{\omega_{0i}(1 + b_{0i})} \ln \left[ \frac{v_i^{(\sigma)}}{v_i^{(\alpha)}} \left( \frac{a_i^{(\alpha)}}{a_i^{(\beta)}} \right)^{\rho_{0i}} \right], \tag{4} \]

where \( \sigma_{0i} = \sigma_{0ix}(1 + b_{0i})^{-1} \), \( b_{0i} = \frac{2}{r} \left( v_{0i}^{(\sigma)} - \rho_{0i} v_{0i}^{(\beta)} \right) \left( r \omega_{0i} \right)^{-1} \), \( \rho_{0i} = \left( v_{0i}^{(\sigma)} - v_{0i}^{(\alpha)} \right) \left( v_{0i}^{(\beta)} - v_{0i}^{(\alpha)} \right)^{-1} \), \( \sigma_{0ix} \) is the interfacial tension at the boundary of \( \alpha \) and \( \beta \) phase for \( i \)-th component.

The equation which has been received in [7] and which has been taken into account at the derivation of the equation (4) follows from the eq.(3) at \( r=\infty \). If to assume, that coefficients of activity are equal to unity in all phases ( \( f_i^{(\xi)} = 1 \), \( \xi=\alpha,\beta,\sigma \) ), the equation of the interface tension isotherm for the curved boundary obtained in [1] follows from the equation (4). For a disperse particle (phase \( \alpha \)) of radius \( r \) (a drop or a solid particle) in a vapor phase (phase \( \beta \)) \( \rho_{0i} \to 0 \) and from the equation (4) we obtain

\[ \sigma = \sigma_{0i} + \frac{RT}{\omega_{0i}(1 + b_{0i})} \ln \frac{a_i^{(\sigma)}}{a_i^{(\alpha)}}, \tag{5} \]

which is an analogue of Butler’s equation for the case of the curved boundaries.

It can be shown [1], that

\[ b_{0i} = \frac{v_{0i}^{(\sigma)} - \rho_{0i} v_{0i}^{(\beta)}}{\omega_{0i}} = \frac{2 \delta_{0i}}{r} \left[ 1 + \frac{\delta_{0i}}{r} + \frac{1}{3} \left( \frac{\delta_{0i}}{r} \right)^2 \right], \tag{6} \]

where \( \delta_{0i} \) is Tolmen’s length.

No restrictions have been applied in derivation of eq.(4) on the value of curvature radius. This is correct for separately taken nanoparticles (in the own vapor) or nanoparticles immersed in various dispersive mediums (phase \( \beta \)). The restriction on values \( r \) is connected to the equilibrium condition of \( \alpha \) and \( \beta \) bulk phases that assumes the existence of a formation possessing properties of a phase \( \alpha \) of the boundary with other phase of the macroscopic size (\( \beta \)) through the non-homogeneous transition layer. At \( 2 \delta_{0i}(r)^{-1} << 1 \) the equation of the interface tension isotherm looks like

\[ \sigma = \sigma_{0i} + \frac{RT}{\omega_{0i}(1 + 2 \delta_{0i}/r)} \ln \left[ \frac{a_i^{(\sigma)}}{a_i^{(\alpha)}} \left( \frac{a_i^{(\alpha)}}{a_i^{(\beta)}} \right)^{\rho_{0i}} \right], \tag{7} \]

where

\[ \sigma_{0i} = \sigma_{0ix} \left( 1 + \frac{2 \delta_{0i}}{r} \right)^{-1}. \tag{8} \]

Let us consider the interfacial tension isotherm at the curved boundary in binary system under the constant external pressure in the dispersive medium that often takes place in practice. In this case the relation (2) yields

\[ \sigma = \sigma_{0i} + \frac{RT}{\omega_{0i}(1 + m_{0i})} \ln \frac{a_2^{(\sigma)}}{a_2^{(\alpha)}}, \tag{9} \]

where \( \sigma_{0i} = \sigma_{0ix}(1 + m_{0i})^{-1} \), \( m_{0i} = b_{0i} + \frac{2 \rho_{0i} v_{0i}^{(\alpha)}}{r \omega_{0i}} \).
In derivation of eq.(9) it has been taken into account that \( r=\infty \), and hence, \( p^{(\alpha)} = p^{(\beta)} = p \) and an additional condition \( p=\text{const} \) takes place. Then we got
\[
\sigma_x = \sigma_{0x} + \frac{RT}{\omega_{0i}} \ln \frac{a_{2x}^{(\sigma)}}{a_{2x}^{(\alpha)}}.
\]  
Under the conditions \( T=\text{const} \) and \( p^{(\mu)}=\text{const} \) one can obtain from (9) the dimensional dependence of the interfacial tension in one-component system
\[
\sigma_0(r) = \sigma_{0/n} \left[ \frac{2\delta_{0i}}{r} \left( 1 + \frac{\delta_{0i}}{r} + \frac{1}{3} \frac{\delta_{0i}^2}{r^2} \right) + \frac{2}{r} \frac{\rho_{0i} v^{(\sigma)}_{0i}}{\omega_{0i}} \right]^{-1}
\]  
For a disperse particle at the boundary of vapor (\( \rho_{0i} \to 0 \)), the denominator in (11) coincides with expression (6).

3. Conclusions
- Within the framework of a rigid transition layer model the equation of the interfacial tension isotherm in the binary system consisting of a disperse particle and a dispersive medium has been obtained with regard for particles interactions.
- The relation connecting an interfacial tension on curved boundary with characteristics of a transitive layer and a disperse particle under the constant pressure condition in the dispersive medium is derived.
- Butler's formula for a surface tension and some other relations follow from the obtained equations under corresponding conditions as well as the well known expressions for the interfacial tension including Tolmen’s formula for one-component systems.

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