Surface-induced shift of melting/freezing temperatures at interfaces between two semi-infinite media

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Many physical properties and the structure of liquids at interfaces differ from those of the same liquids in the bulk state. In particular, the freezing temperatures of numerous liquid systems at interfaces between two fluids can be either increased or decreased compared to the temperature of corresponding bulk phase transition. The approach proposed in this paper allows one to predict the surface-induced shift of the melting/freezing temperatures in various systems.

Key words: interfaces, surface forces, phase transitions.

Melting belongs to the simplest first-order phase transitions that most frequently occur in nature. Theoretical and experimental investigations of this phenomenon have been carried out through the ages. Recently, interest in research in this field has been grown significantly due to the obtaining of new experimental data on phase transitions at interfaces. For instance, in addition to the known phenomenon called the pre-melting of ice,[1,2] the existence of a quasi-liquid layer at the solid—vapor interface at temperatures below the bulk melting temperature was reported for metals,[3—5] solid inert gases,[6] semiconductors,[7] and polymers.[8] In contrast to this, the alkane—vapor,[9] alcohol—vapor,[10] and alcohol—water[11,12] systems including a broad range of hydrocarbons and alcohols, as well as the surfactant adlayers at alkane—water interfaces[13,14] show freezing of the surface layers/adlayers at temperatures above the bulk phase transition temperature.

Various theoretical approaches were proposed to explain these features of the phase transitions at interfaces between two media. For instance, the theory of surface freezing of *n*-alkanes[15] is based on the inclusion of the center-of-mass fluctuations of a long-chain alkane molecule along the molecular axis and, correspondingly, fluctuations of the mutual arrangement of methyl groups in the neighboring molecules in the surface monolayer. According to calculations,[15] it is these fluctuations that can provide the energetically more favorable (due to the entropy term) quasi-solid state of the alkane monolayer on the surface of a bulk liquid hydrocarbon phase. It should be noted that the entropy mechanism proposed[15] for the liquids with linear chain molecules is inapplicable to the liquids with spherical molecules and requires a significant modification prior to being applied to branched molecules.

Yet another approach to the description of surface melting was developed in a study[16] of surface-induced smectic ordering in the fluid of hard spheres. The ordering exponentially decreases on going into the interior of the bulk phase and causes the appearance of an additional term in the expression for the free energy of the system. This term oscillates upon a change in the distance from the interface and for some systems makes the existence of a liquid layer on the surface of the bulk solid phase at temperatures below the bulk melting temperature energetically favorable. At the same time this approach[16] can not be immediately applied to, *e.g.*, electrolyte solutions or to liquids with non-spherical molecules.

The two methods[15,16] treat the surface melting and surface freezing as phenomena of different physical nature. Using thermodynamic analysis, in this work we will show that both phenomena can be explained from the standpoint of a unified approach based on the inclusion of the effect of the surface forces on the structure of the liquid in the surface layer.

Thermodynamics of the boundary phase

Following the classical studies,[17—19] we will consider a surface layer at the interface between two fluids as a boundary phase. The outer boundaries of this phase separate homogeneous bulk phases from inhomogeneous surface layer. According to the Gibbs integral equation, the

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 1, pp. 14—18, January, 2007.

excess free energy, U^E, of a unit surface area of this phase can be written as follows

$$U^E = TS^E + \gamma + \sum_i \Gamma_i \mu_i, \qquad (1)$$

where T is the absolute temperature, S^E is the excess entropy of the unit surface area, Γ_i are the surface excesses of the solution components, μ_i are the chemical potentials of the solution components, and γ is the energy of formation of the unit surface area; summation is performed over all the solution components. All the surface excesses refer to a certain dividing surface whose position, in the case of a planar boundary, can be chosen arbitrarily. Let this boundary coincide with one of the outer surfaces of the boundary phase, which separates, *e.g.*, the homogeneous bulk phase I and the boundary phase α (Fig. 1). Then one has

$$U^E = U_\alpha - U_{\mathrm{II}}, \qquad S^E = S_\alpha - S_{\mathrm{II}}, \qquad \Gamma_i = n_{\alpha_i} - n_{\mathrm{II}_i}, \qquad (2)$$

where U_α, S_α and n_{α_i} are the internal energy, entropy, and the number of moles of the components in the boundary phase per unit surface area of the boundary phase; U_{II}, S_{II}, and n_{II_i} refer to the same parameters for the equivalent volume of the homogeneous phase II. Let the thickness of the boundary phase be h. Because the Gibbs free energy G_{II} per unit surface area of the interface written for phase II is given by

$$G_{\mathrm{II}} = \Sigma n_{\mathrm{II}_i}\mu_i = U_{\mathrm{II}} - TS_{\mathrm{II}} + Ph \qquad (3)$$

(P is the pressure in the system), one gets

$$\gamma = U_\alpha - TS_\alpha + Ph - \Sigma n_{\alpha_i}\mu_i. \qquad (4)$$

The Gibbs free energy per unit surface area of the boundary phase can be calculated using the following equation

$$G_\alpha = \Sigma n_{\alpha_i}\mu_i. \qquad (5)$$

It should be noted that constancy of the chemical potentials of the components in different regions of the compositionally and structurally inhomogeneous boundary phase α is held due to the presence of a nonuniform external field (here, this role is played by the macroscopic field of surface forces). This field decreases into the interior of each phase along the normal to the interface and is uniform in the cross sections parallel to the interface.

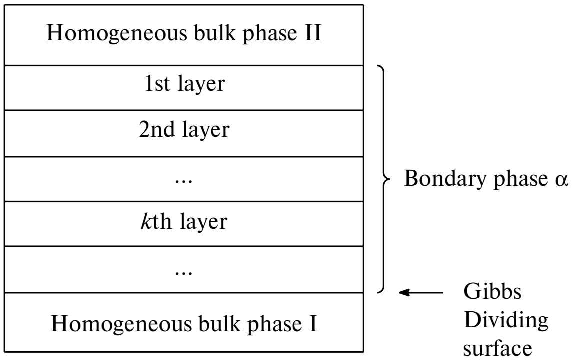

Fig. 1. Scheme of the system under study.

Assuming a constant composition and structure of the boundary phase with no field of surface forces, the following relationships are valid for the Gibbs free energy of this phase ($G_\alpha{}'$)

$$G'_\alpha = U_\alpha - TS_\alpha + Ph = \int_h \rho_{\alpha_i}(z)\lambda_i(z)\mathrm{d}z, \qquad (6)$$

where $\rho_{\alpha_i}(z)$ is the density of the ith component in the boundary phase, $\lambda_i(z)$ are the coordinate-dependent (because of inhomogeneous structure) chemical potentials of the components in the boundary phase in the absence of the field of surface forces, the z axis is oriented normal to the interface, and integration is performed over the whole thickness, h, of the boundary phase. For brevity, in the text below this phase will be called the reference phase. By dividing the reference phase into sublayers characterized by constant $\lambda_i(z)$ values from Eq. (6) one gets

$$G'_\alpha = \sum_{i,k} n_{ik}\lambda_{ik}, \qquad (7)$$

where k is the sublayer number.

With allowance for expression (7), relation (4) takes the form

$$\gamma = \sum_{i,k} n_{ik}(\lambda_{ik} - \mu_i). \qquad (8)$$

Clearly, because of rapid decrease in the field of surface forces one has $\lambda_{ik} \to \mu_i$ at large k values and only a finite number of the surface sublayers contribute to the Gibbs free energy of formation of the unit surface area.

Assuming that the boundary phase is one monolayer thick, expression (8) is reduced to the equation first derived by A. A. Zhukhovitskii[19] based on the consideration similar to our treatment:

$$\gamma = \sum_i n_i(\lambda_i - \mu_i). \qquad (9)$$

Since in this work we are interested in the phase transitions at interfaces in one-component systems, expression (8) can be re-written in a simpler form:

$$\gamma = \sum_k n_k(\lambda_k - \mu) = \sum_k \gamma_k, \qquad (10)$$

where γ_k is the contribution of the corresponding sublayer of the boundary phase to the energy of formation of the unit surface area of the interface. Note that because of the nonequilibrium state of the reference phase one always has $\lambda_k > \mu$ and each term in expression (10) is nonnegative.

The following should be pointed out prior to considering phase transitions in different layers of the boundary phase. Because the reference phase was chosen in such a manner that its composition and structure in each layer at all temperatures be the same as the composition and structure of the corresponding layer in the real boundary phase, the transition temperature for the kth sublayer of the reference phase and for the coresponding sublayer of the phase α are the same. This is a consequence of unambiguous relation between the phase state of a substance and its temperature and density at a given pressure. Thus on the one hand, to study a phase transition in the kth sublayer of the real boundary phase, it is sufficient to study the phase transition in the corresponding sublayer of the reference phase, considering the latter as a region of a certain bulk phase. On the other hand, inhomogeneous structure of the boundary phase leads to a sequence of phase transitions as the temperature of the system approaches the bulk transition temperature and the structure of the boundary sublayers matches the structure of the bulk phase.

Treating the vapor of the component under study as an ideal gas, one can relate the corresponding chemical potentials to the vapor pressure:

$$\mu = \bar{\mu} + RT\ln p^0, \tag{11}$$

$$\lambda_k = \bar{\mu} + RT\ln p_k^{\alpha}, \tag{12}$$

where $\bar{\mu}$ is the temperature-dependent standard chemical potential independent of the state of the component under study;[17] $p_k{}^{\alpha}$ is the vapor pressure corresponding to the equilibrium between the vapor and the volume element of the bulk liquid characterized by the chemical potential λ_k. From relations (11) and (12) one gets

$$p_k{}^{\alpha} = p^0\exp[(\lambda_k - \mu)/(RT)] = p^0\exp[\gamma_k/(n_kRT)]. \tag{13}$$

From Eq. (13) and the non-negativity of γ_k values it folows that the vapor pressure corresponding to the equilibrium between the vapor and any sublayer of the reference phase should not be less than the vapor pressure over the initial bulk phase (*i.e.*, $p_k{}^{\alpha} > p^0$ at $\gamma_k > 0$). Relation (13) is in fact the equation of state for the kth surface sublayer and can be written for both the liquid (L) and the solid (S) states of this sublayer:

$$p_{k(\mathrm{L})}^{\alpha} = p_{(\mathrm{L})}^{0}\exp[\gamma_{k(\mathrm{L})}/(n_{k(\mathrm{L})}RT)],$$
$$p_{k(\mathrm{S})}^{\alpha} = p_{(\mathrm{S})}^{0}\exp[\gamma_{k(\mathrm{S})}/(n_{k(\mathrm{S})}RT)]. \tag{14}$$

Now we will use the fact that the change in the vapor pressure over the liquid and solid obeys the Clausius—Clapeyron equations. Following the classical tradition, we will assume that they are also valid for the metastable states, namely, a superheated solid or a supercooled liquid:

$$\frac{\mathrm{d}\ln p_{(\mathrm{L})}^{0}}{\mathrm{d}T} = \frac{L_{\mathrm{LV}}}{RT^2}, \qquad \frac{\mathrm{d}\ln p_{(\mathrm{S})}^{0}}{\mathrm{d}T} = \frac{L_{\mathrm{SV}}}{RT^2}, \tag{15}$$

where L_{LV} and L_{SV} are the molar heats of vaporization and sublimation, respectively. From relations (15) it follows that

$$\frac{\mathrm{d}\ln\left(p_{(\mathrm{L})}^{0}/p_{(\mathrm{S})}^{0}\right)}{\mathrm{d}T} = -\frac{q}{RT^2}. \tag{16}$$

Here $q = L_{\mathrm{LV}} - L_{\mathrm{SV}}$ is the latent heat of melting of the bulk phase. By integrating Eq. (16) from the melting temperature of the kth sublayer in the boundary phase ($T_k{}^{\mathrm{sf}}$) to the bulk melting temperature T^{bf} with allowance for relationship (13) and using the following expressions

$$p_{(\mathrm{L})}^{0} = p_{(\mathrm{S})}^{0} \text{ at } T = T^{\mathrm{bf}},$$
$$p_{k(\mathrm{L})}^{\alpha} = p_{k(\mathrm{S})}^{\alpha} \text{ at } T = T_k{}^{\mathrm{sf}}, \tag{17}$$

we eventually get for the shift of the melting temperature of the kth sublayer in the boundary phase

$$\Delta T_k = T^{\mathrm{bf}} - T_k^{\mathrm{sf}} = \frac{T^{\mathrm{bf}}}{q}\left[\frac{\gamma_{k(\mathrm{S})}}{n_{k(\mathrm{S})}} - \frac{\gamma_{k(\mathrm{L})}}{n_{k(\mathrm{L})}}\right]_{T=T_k^{\mathrm{sf}}}. \tag{18}$$

From Eq. (10) it follows

$$\gamma_{k(\mathrm{S,L})} = \gamma_{(\mathrm{S,L})} - \sum_{j\neq k}\gamma_{j(\mathrm{S,L})}. \tag{19}$$

Then one has

$$\Delta T_k = \frac{T^{\mathrm{bf}}}{q}\left[\frac{\gamma_{(\mathrm{S})}}{n_{k(\mathrm{S})}} - \frac{\gamma_{(\mathrm{L})}}{n_{k(\mathrm{L})}} - \sum_{j\neq k}\left(\frac{\gamma_{j(\mathrm{S})}}{n_{k(\mathrm{S})}} - \frac{\gamma_{j(\mathrm{L})}}{n_{k(\mathrm{L})}}\right)\right]_{T=T_k^{\mathrm{sf}}}. \tag{20}$$

The simplest case to be analyzed is to consider the boundary phase, which is at most one monolayer thick due to rapid decrease in the field of surface forces. Numerous experiments showed[9,20,21] that this is the case for n-alkanes at the interfaces with their own vapors. Here, expression (20) is simplified:

$$\Delta T_1 = \frac{T^{\mathrm{bf}}}{q}\left[\frac{\gamma_{(\mathrm{S})}}{n_{\alpha(\mathrm{S})}} - \frac{\gamma_{(\mathrm{L})}}{n_{\alpha(\mathrm{L})}}\right]_{T=T_1^{\mathrm{sf}}}. \tag{21}$$

From Eq. (21) it follows that the shift of the melting temperature of the surface monolayer toward higher temperatures will unambiguously occur if the following conditions are met simultaneously:

$$\gamma_{\mathrm{S}} < \gamma_{\mathrm{L}}, \qquad n_{\alpha(\mathrm{S})} > n_{\alpha(\mathrm{L})}. \tag{22}$$

The second inequality in (22) means that the surface area per molecule in the liquid monolayer is larger than in the solid. Seemingly, it is this situation that is typical of *n*-alkanes. Assuming that the surface energy of the bulk solid phase at the bulk melting temperature equals the surface tension of the liquid covered with the frozen monolayer at the same temperature, from Ref. 9 it follows that for alkanes with $16 \le m \le 50$ (m is the number of carbon atoms) one has $\gamma_S < \gamma_L$. The melting of bulk alkanes is accompanied by an increase in the molar volume.[22] Additionally, SFG spectroscopy data[23] obtained in a study of the *n*-alkane surface layers point to structural similarity between the surface monolayers in the solid and liquid states. The molecules show a trend to have their long axes oriented normal to the interface. Here, the liquid monolayer is characterized by a larger number of *gauche*-conformations, whereas the molecules in the solid monolayer mainly adopt the transplanar configuration. These facts indicate an increase in the molar volume of the surface monolayer upon melting. Because exact values of the surface areas per alkane molecule in the surface monolayers are unavailable, we will calculate the shift of the melting temperature of the surface monolayer using relationship (21) with allowance for the relation between the molar volume v, monolayer thickness h, and the number of molecules per unit surface area $n = h/v$, and using the data for bulk alkanes.[22,24,25] The monolayer thicknesses (assuming their independence of the phase state of the monolayer) were taken from Ref. 9. The results of calculations and the experimental values[9] are plotted in Fig. 2. Incompleteness of the available experimental data on the heats of melting, melting temperatures, and the shift of the melting temperatures in the surface layer precluded calculations for the whole alkane homologous series. Additionally, the data reported by different authors for the same compounds are significantly different (see, *e.g.*, the latent heats of melting[25,26] and the freezing temperatures of the surface layer of alkanes at interfaces with the gaseous phase[9,21]). Therefore, agreement between the theoretical and experimental ΔT^{sf} values plotted in Fig. 2 (correlation coefficient is 0.78) can be considered as satisfactory. At the same time, Fig. 2 shows a trend to overestimation of the ΔT^{sf} values obtained from calculations using Eqn. (21) compared to experimental data. Apparently, this is a consequence of the use of the parameters characterizing the bulk solid and liquid states instead of the corresponding parameters of the monolayer.

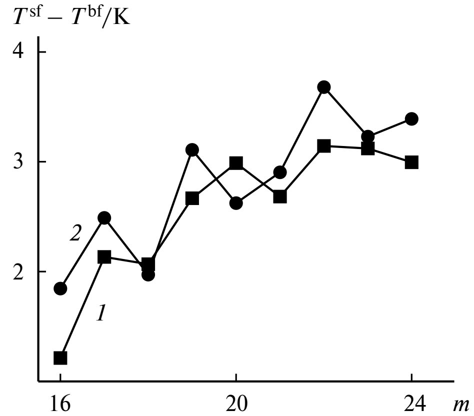

Fig. 2. Experimental[9] (*1*) and theoretical (*2*) calculated on the basis of Eq. (21) shifts of the melting temperature of the monolayer surface relative to the melting temperature of the bulk phase for alkanes with different number of carbon atoms (m).

Therefore, it was appropriate to solve an inverse problem, namely, to estimate the change in the molar volume upon melting of the surface monolayer using experimental data on the shift of the melting temperature. The molar volume of the solid monolayer was taken equal to the molar volume of the solid rotator phase (see Ref. 9). The results of calculations and the experimental values[24] are plotted in Fig. 3. Although, for the reasons discussed above, the scatter of the theoretical f values ($f = v_{\alpha(S)}/v_{\alpha(L)}$) is rather large, the average value of this ratio ($f = 1.09$) for the alkanes containing from 16 to 24 carbon atoms is smaller than the corresponding value characteristic of the bulk phases ($f = 1.11$).[22] Therefore, the liquid in the monolayer has a higher density compared to the bulk phase. The results obtained are in good agreement with the published data[23] that indicate a quasi-solid ordering of the liquid in the surface layer.

The shift of the melting temperature of the monolayer can also be unambiguously determined if the following conditions are simultaneously met:

$$\gamma_S > \gamma_L, \qquad n_{\alpha(S)} < n_{\alpha(L)}. \qquad (23)$$

In the systems that obey the inequalities (23) the melting temperature of the surface monolayer is lower than in the bulk phase (pre-melting of the surface layer should occur). The system water—water vapor is one of the best known systems of this type.[27] Indeed, experimental

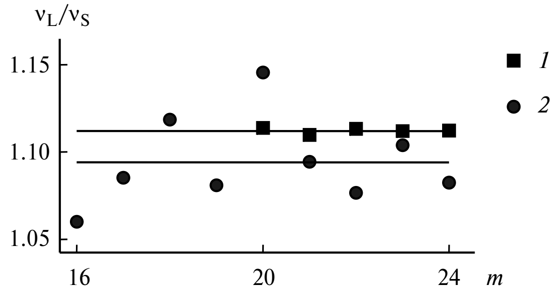

Fig. 3. Relative change in the molar volume at melting of the bulk phase (*1*) and surface monolayer (*2*) on the number of carbon atoms in alkane molecule (m). Data for the surface monolayer were calculated using relationship (21), those for the bulk phases were taken from Ref. 24. Lines correspond to average values.

methods indicate[1] the existence of a liquid water layer on the surface of ice at temperatures well below 0 °C. However, water forms a multilayer boundary phase;[28] therefore, the shifts of the transition temperatures in the surface layers should be estimated from relationship (20). It should be noted that evaluation of the γ_k parameters appeared in this expression is impossible in the framework of thermodynamics and requires the use of other methods. Nevertheless, the approach proposed in this work for multilayer boundary phases makes it possible to establish the sign of the shift of the melting temperature of the surface layers compared to the melting of bulk phases.

If the substances under study are not described by the systems of inequalities (22) or (23), the sign of the shift of the melting temperature of the surface monolayer can be determined by the ratio of the parameters $\gamma_S/n_{\alpha(S)}$ and $\gamma_L/n_{\alpha(L)}$ (this follows from Eq. (21)). For instance, the γ_S values of alkanes with $m \le 14$ carbon atoms become larger than γ_L,[9] although the condition $n_{\alpha(S)} > n_{\alpha(L)}$ is met. As a result, no surface freezing at the alkane—vapor interface is observed for these compounds in contrast to the higher alkanes (alkanes with larger *m* values).

Now we will consider yet another example illustrating specific features of melting/freezing at gas—metal interfaces. Many metals (*e.g.*, Al,[29] Cu,[5] Pb [4]) are characterized by pre-melting on the non-close-packed faces (110), (221), and (332), whereas the close-packed (111) faces undergo equilibrium melting only at the bulk melting temperatures. The approach proposed in this work implies the use of relationship (20) for analysis of the sigh of the shift of the melting temperature for the boundary phase. For instance, from the fact that the shift of the melting temperature calculated for the Pb (111) face approaches zero and from the physically substantiated assumption that all terms in the sum in relationship (20) have the same sign it follows that $\gamma_S/n_{k(S)} \approx \gamma_L/n_{k(L)}$ and $\gamma_{j(S)}/n_{k(S)} \approx \gamma_{j(L)}/n_{k(L)}$ for all *k* and *j*. Transition to looser-packed crystal faces, on the one hand, causes a decrease in $n_{k(S)}$. On the other hand, the $\gamma_S(\theta)/\gamma_S(111)$ ratio increases in the order (111), (332), (221), (110),[30] thus indicating an increase in γ_S for the corresponding face. Thus, the first term in parentheses in expression (20), which determines the sign of the shift of the melting temperature of the boundary phase, becomes positive and increases in the same order, thus providing an explanation for the experimentally observed pre-melting on the (332), (221), and (110) faces. Our qualitative analysis shows that the maximum shift of the pre-melting temperature on these faces should occur for the (110) face. This is in excellent agreement with experimental data.[4,31]

Summing up, the thermodynamic approach proposed in this work is based on the inclusion of the effect of the surface forces on the structure of the liquid in the surface layer. These forces make the structure of the boundary phase inhomogeneous and the properties of this phase different from those of the bulk phase. Additionally, the surface forces cause the first-order phase transition temperature to shift because of unambiguous relation between the phase state of a compound and its temperature and composition at a given pressure. In the case of multilayer boundary phases, structural unhomogeneity of these systems can in turn be a reason for a sequence of phase transitions in particular boundary sublayers as the temperature of the system approaches the bulk transition temperature.[32] Finally, in some systems containing anisotropic molecules the surface forces can induce orientation phase transitions.[33]

This work was financially supported by the Russian Foundation for Basic Research (Project No 06-08-00488).

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Received September 11, 2006;
in revised form November 9, 2006