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RHEOLOGICAL AND THERMAL PROPERTIES OF THE SURFACE LAYER OF LIQUIDS

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A grid model of the surface liquid layer at the boundary with the gas and its rheological and thermophysical properties (temperature dependence of the surface tension and surface heat capacity) have been described. It has been obtained that the mole heat capacity of the surface layer is nearly the same (5.6 J/(mole·K)) for many liquid metals. It has been shown that for calculation of the rheological properties it is expedient to use the Kelvin model.

The macroscopic theory of capillary phenomena that was created by Laplace and Young 200 years ago is based on the following hypothesis on the mechanical properties of the surface layer of a liquid at the boundary with the gas: the surface layer is considered as a very thin elastic shell, i.e., represents a solid body in mechanical properties [1]. Fundamental laws of capillarity theory — capillary pressure determined by the surface tension and the curvature of the liquid surface and boundary wetting angle of solid surfaces — were derived based on the solid-phase surface-layer model.

This theory has been confirmed by numerous experiments performed with different liquids and solid bodies. It is widely and successfully used for solution of many applied problems (heat and mass exchange, behavior of a liquid in weightlessness, powder metallurgy, ore flotation, oil production, and others). However, the macroscopic problems of capillarity theory, particularly the structure of the surface liquid layer, remain just as topical as before and are being intensely studied theoretically (with the use of computational methods) and experimentally; this has become possible owing to the appearance of high-resolution methods. Below, we consider a grid model (proposed recently) of the surface layer and its rheological and thermophysical properties.

The grid surface-layer model is as follows [2, 3]: the surface layer of a pure liquid at the boundary with the gas consists of two phases. One phase (the solid one) is represented by fine one-dimensional (fiber-like) nanoparticles; the fibers form a unified grid.

The fibers possess mechanical strength determined by the elastic modulus of a given substance. Therefore, the grid ensures one basic capillary property of the liquid: a definite (spherical) shape of small droplets whose radius is $r < a$, where

$$a^2 = 2\gamma/\rho_{\text{liq}}g \,. \tag{1}$$

Owing to the extremely small thickness, the grid fibers are capable of experiencing large elastic (reversible) strains much larger than the elastic limit strains of massive solid bodies. In this sense, we may speak of the fact that the surface liquid layer possesses superelasticity.

The other phase of the surface layer in the grid model is the liquid in closed cells formed by the grid nodes. Thus, the surface layer in the grid model may be described using the Kelvin rheological model: a parallel connection of the elastic element (grid fibers with elastic modulus E) and the viscous element (Newtonian liquid with a viscosity η in the grid cells).

The relative fraction φ occupied by the grid fibers on the surface depends on the temperature T: at the melting temperature T_{m}, we have $\varphi \to 1$; with increase in the temperature, φ decreases ($d\varphi/dT < 0$). In the vicinity of the critical temperature, the grid ceases to be unified (bound into a unified structure), i.e., the value of φ becomes lower

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than the corresponding percolation threshold. The temperature dependence of the surface tension $\gamma = f(T)$ of pure liquids is quite easily and clearly explained in this context. It has experimentally been established that, as the temperature increases, (liquefied inert gases, organic substances, water, and molten metals), the surface tension decreases for all substances ($d\gamma/dT < 0$), whereas the temperature coefficients of surface tension $\alpha = d\gamma/dT$ for all the substances lie in a comparatively narrow range: $\alpha = -(0.1\text{–}0.2)$ mJ/(m^2·K) [4].

The grid model is also consistent with a well-known regularity — a decrease in the surface tension of solutions with increase in the concentration of surfactants: $d\gamma/dc < 0$. Within the framework of this model, the influence of surfactants lies in the fact that they may keep the grid from "cross-linking," i.e., may hinder the formation of its nodes. Accordingly, the work expended on extending such an "imperfect" grid decreases; therefore, the surface tension decreases with growth in the concentration of surfactants in the surface layer (specific adsorption).

The most controversial aspect of the grid model is the possibility of forming a stable solid phase in the surface liquid layer, since the temperature of the liquid is higher than the melting point T_{m} ($T > T_{\mathrm{m}}$). In addition to the arguments given above, this model is supported by the recent investigations of the surface structure of liquids (high homologs of saturated hydrocarbons, certain alcohols, mercury, and gallium) by the highly sensitive method of small-angle x-ray scattering of liquid layers of molecular thickness [5–7]. The main result of these investigations is that, at temperatures 3 to 4$^{\mathrm{o}}$C higher than the melting point, the surface layer of thickness $(1\text{–}2)d$ represents a two-dimensional crystalline structure; its lattice is different in parameters from the corresponding lattice of the volumetric solid phase of a given substance.

Another (macroscopic) confirmation of the grid model is that the surface tension of many atomic liquids in the vicinity of the melting temperature is in direct proportion to the melting heat Q_{m} [8].

Let us pass to consideration of the thermophysical properties of the surface layer based on the grid model. We consider the thermal balance of the isothermal process of formation of the liquid surface at the boundary with the gas upon the separation of a certain macroscopic liquid volume into two parts. In accordance with the thermodynamics of surface phenomena, the work expended on this process per unit area represents the specific internal energy ε of the phase interface. Due to the excess of the energy ε, the state of the surface layer at the instant of its formation turns out to be nonequilibrium in relation to the internal volume of the liquid. The excess energy may be released with liberation of the heat ΔQ in accordance with the first law of thermodynamics $\Delta Q = \varepsilon$.

In turn, we recognize two successive processes of heat liberation:

1. Adiabatic cooling of the surface layer from the initial temperature T to the melting temperature of a given substance. The heat

$$\Delta Q_1 = C_{\mathrm{s}}\,(T - T_{\mathrm{m}}) \tag{2}$$

will be liberated.

2. Solidification of the surface layer at the melting temperature T_{m} with the liberation of the heat

$$\Delta Q_2 = \varphi Q_{\mathrm{m}} \rho_{\mathrm{sol}} \delta\,. \tag{3}$$

From the conditions $\Delta Q = \Delta Q_1 + \Delta Q_2$ and $\varepsilon = \Delta Q$, we obtain the equation of thermal balance of the surface layer

$$\varepsilon = C_{\mathrm{s}}\,(T - T_{\mathrm{m}}) + \varphi Q_{\mathrm{m}} \rho_{\mathrm{sol}} \delta\,. \tag{4}$$

Hence the fraction of the area φ that is occupied by the grid is

$$\varphi = \frac{\varepsilon - C_{\mathrm{s}}\,(T - T_{\mathrm{m}})}{Q_{\mathrm{m}} \rho_{\mathrm{sol}} \delta}\,. \tag{5}$$

Thus, this fraction linearly decreases with increase in the liquid temperature, which is consistent with the experimental dependences of the surface tension on temperature (see above).

TABLE 1. Mole Surface Heat Capacities C_s^M of Liquid Metals

Metal	$-\alpha$, mJ/(m^2·K)	δ, nm	C_s^M, kJ/(mole·K)
Li	0.14	0.35	5.2
Na	0.10	0.43	5.5
K	0.065	0.27	5.5
Rb	0.06	0.57	5.9
Cs	0.05	0.62	5.3
Cu	0.24	0.29	5.7
Ag	0.18	0.32	5.8
Au	0.17	0.32	5.9
Fe	0.23	0.29	5.6
Pb	0.12	0.39	5.2
Al	0.15	0.32	4.6
Sn	0.09	0.38	3.9
Ba	0.08	0.63	8.3
Hg	0.20	0.37	8.0

The equation of thermal balance of the surface layer (4) has the following physical meaning. Part of the work ε of formation of a unit area of the liquid surface, which is equal to $C_s(T - T_m) = \Delta Q_1$, is expended on cooling the surface layer. The other part of this work ($\varphi Q_m \rho_{sol} \delta = \Delta Q_2$) is expended on forming the grid. It is precisely this term that determines the surface of the liquid γ, since all the methods of its measurement are tensiometric (mechanical) [9]. By definition, the surface tension γ represents the mechanical work necessary for increasing the surface per unit area. Hence we obtain

$$\gamma = \varphi Q_m \rho_{sol} \delta . \tag{6}$$

With account for (6), the equation of thermal balance of the surface layer (4) takes the form

$$\gamma = \varepsilon - C_s (T - T_m) , \tag{7}$$

whence we may find the temperature coefficient of surface tension:

$$\frac{d\gamma}{dT} = - C_s . \tag{8}$$

The values of $d\gamma/dT$ have been determined experimentally for many liquids of different chemical nature [4]. Therefore, Eq. (8) enables us to calculate an important thermal characteristic of the surface layer: its heat capacity C_s. Hence, in turn we may find the mole surface heat capacity

$$C_s^M = \frac{C_s}{\rho_{sol} \delta} M . \tag{9}$$

Table 1 gives results of calculations of the mole surface heat capacity for 14 liquid metals. It has been assumed that the surface-layer thickness is $\delta = d$.

The basic conclusion is that the mole heat capacities of the surface layer are very similar for most liquid metals. For ten metals, from lithium to lead, the average value is $C_s^M = (5.6 \pm 0.1)$ J/(mole·K). This regularity is analogous to the well-known law of Dulong and Petit: the mole heat capacity of solid metals is the same (~6 J/(mole·K)) at fairly high temperatures.

NOTATION

a^2, capillary constant of the liquid, m^2; c, concentration, $mole/m^3$; C_s, specific heat of the surface liquid layer, $J/(m^2 \cdot K)$; C_s^M, mole heat capacity of the surface liquid layer, $J/(mole \cdot K)$; d, atomic (molecular) diameter, m; E, elastic modulus, Pa; g, free-fall acceleration, m/sec^2; M, molecular weight; ΔQ_1, specific heat liberated in cooling of the surface layer, J/m^2; ΔQ_2, specific heat liberated in solidification of the surface layer, J/m^2; Q_m, melting heat, J/kg; r, radius of curvature, m; T, temperature, K; α, temperature coefficient of surface tension, $J/(m^2 \cdot K)$; γ, surface tension of the liquid, J/m^2; δ, thickness of the surface liquid layer, m; ε, specific internal energy of the liquid surface, J/m^2; η, liquid viscosity, Pa·sec; ρ_{liq}, liquid density, kg/m^3; ρ_{sol}, solid-phase density, kg/m^3; φ, fraction of the area occupied by solid particles on the liquid surface. Subscripts and superscripts: liq, liquid; m, melting; M, mole; s, surface; sol, solid.

REFERENCES

1. J. S. Rowlinson and B. Widom, in: *Molecular Theory of Capillarity* [Russian translation], Mir, Moscow (1986), pp. 14–38.
2. B. D. Summ, Grid model of the liquid surface layer, *Vestn. Mosk. Univ.*, Ser. 2, *Khimiya*, **34**, No. 1, 59–66 (1993).
3. B. D. Summ, Structure of the liquid surface layer (the "grid" hypothesis), *Ross. Khim. Zh.*, **38**, No. 6, 19–23 (1994).
4. I. S. Grigor'ev and E. Z. Meilikhov (Eds.), in: *Physical Quantities: Handbook*. Ch. 14. *Surface Tension* [in Russian], Energoatomizdat, Moscow (1991), pp. 330–337.
5. O. M. Magnussen, B. M. Ocko, M. J. Regan, et al., X-ray reflectivity measurements of surface layering in liquid mercury, *Phys. Rev. Lett.*, **74**, No. 22, 4444–4447 (1995).
6. M. J. Regan, E. H. Kawamoto, S. Lee, et al., Surface layering in liquid gallium: An x-ray reflection study, *Phys. Rev. Lett.*, **75**, No. 13, 2498–2501 (1995).
7. M. Deutsch, X. Z. Wu, E. B. Sirota, et al., Crystalline bilayers on the surface of molten alcohol, *Europhys. Lett.*, **30**, No. 5, 283–288 (1995).
8. B. D. Summ, Empirical correlations of the surface tension of liquid metals with the velocity of sound and the Planck constant, *Vestn. Mosk. Univ.*, Ser. 2, *Khimiya*, **93**, No. 1, 44–47 (2002).
9. A. I. Rusanov and V. A. Prokhorov, *Interphase Tensiometry* [in Russian], Khimiya, St. Petersburg (1994).