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Surface energy and surface tension of liquid metal nanodrops

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Abstract. A unitary approach has been proposed for the calculation of surface energy and surface tension of nanoparticle being in equilibrium with its saturated vapor on both flat and curved surfaces at given temperature. The final equations involve parameters dependent on the type of premelting structure: bcc, fcc or hcp.

The surface energy $\bar{u}$ and the surface tension σ are the most important thermodynamic characteristics of the layer between the coexistent phases. These quantities, in turn, allow one to obtain other characteristics of the interface boundaries such as work of adhesion, edge angle of wetting, coefficient of spreading etc. The values of $\bar{u}$ and σ are of special interest when studying the properties of nanoobjects (particles, bubbles, thin films) because the increase of surface contribution to the properties of the whole system becomes intrinsic.

This communication deals with the calculation of surface energy and surface tension of nanoparticle held in equilibrium with its saturated vapor at constant temperature on the basis of proposed unitary approach.

Let the nanoparticle be sphere of radius r corresponding to the equimolar dividing surface at which the autoadsorption, as known, is nil ($\tilde{A} = \bar{N}/\omega_e = 0$, $\bar{N} = 0$ - number of excess particles, ω_e - molar area).

The surface energy and surface tension shall be the excess energy $\bar{u}_e$ and excess free energy $\bar{F}_e$ per unit area of equimolar dividing surface respectively:

$$\bar{u} = \frac{\bar{u}_e}{\omega_e} = \frac{u - u_\upsilon^{(\alpha)} V_{\bar{N}=0}^{(\alpha)} - u_\upsilon^{(\beta)} V_{\bar{N}=0}^{(\beta)}}{\omega_e}, \qquad (1)$$

$$\sigma = \frac{\bar{F}_e}{\omega_e} = \frac{F - f_V^{(\alpha)} V_{\bar{N}=0}^{(\alpha)} - f_V^{(\beta)} V_{\bar{N}=0}^{(\beta)}}{\omega_e}, \qquad (2)$$

where u and F – internal and free energies of the system, $u_\upsilon^{(\alpha)}$ and $u_\upsilon^{(\beta)}$ - densities of energy in bulk phases α and β of volumes $V_{\bar{N}=0}^{(\alpha)}$ and $V_{\bar{N}=0}^{(\beta)}$, located each side from the equimolar dividing surface, $f_V^{(\alpha)}$ and $f_V^{(\beta)}$ - densities of free energy in mentioned phases.

Let us introduce two more dividing surfaces conditioned by

$$\bar{u} = u - u_\upsilon^{(\alpha)} V_{\bar{u}=0}^{(\alpha)} - u_\upsilon^{(\beta)} V_{\bar{u}=0}^{(\beta)} = 0, \qquad (3)$$

$$\bar{F} = F - f_\upsilon^{(\alpha)} V_{\bar{F}=0}^{(\alpha)} - f_\upsilon^{(\beta)} V_{\bar{F}=0}^{(\beta)} = 0, \qquad (4)$$

where $V_{\bar{u}=0}^{(\alpha)}$, $V_{\bar{u}=0}^{(\beta)}$ and $V_{\bar{F}=0}^{(\alpha)}$, $V_{\bar{F}=0}^{(\beta)}$ - volumes of phases appearing after the division of all the system by the surfaces ($V = V_{\bar{u}=0}^{(\alpha)} + V_{\bar{u}=0}^{(\beta)} = V_{\bar{F}=0}^{(\alpha)} + V_{\bar{F}=0}^{(\beta)}$).

Simple transformations of (1) and (2) with account of (3) and (4) bring us to

$$\bar{u} = \left(u_\upsilon^{(\beta)} - u_\upsilon^{(\alpha)}\right) \frac{\Delta V_{eu}}{\omega_e}, \qquad (5)$$

$$\sigma = \left(f_\upsilon^{(\beta)} - f_\upsilon^{(\alpha)}\right) \frac{\Delta V_{eF}}{\omega_e}, \qquad (6)$$

where $\Delta V_{eu} = V_{\bar{N}=0}^{(\alpha)} - V_{\bar{u}=0}^{(\beta)}$, $\Delta V_{eF} = V_{\bar{N}=0}^{(\alpha)} - V_{\bar{F}=0}^{(\alpha)}$ with

$$\Delta V_{eu} = \int_{(V)} \left[\frac{\rho(z) - \rho^{(\beta)}}{\rho^{(\alpha)} - \rho^{(\beta)}} - \frac{u_\upsilon(r) - u_\upsilon^{(\beta)}}{u_\upsilon^{(\alpha)} - u_\upsilon^{(\beta)}} \right] d\vec{r}, \qquad (7)$$

$$\Delta V_{eF} = \int_{(V)} \left[\frac{\rho(z) - \rho^{(\beta)}}{\rho^{(\alpha)} - \rho^{(\beta)}} - \frac{f_\upsilon(r) - f_\upsilon^{(\beta)}}{f_\upsilon^{(\alpha)} - f_\upsilon^{(\beta)}} \right] d\vec{r}. \qquad (8)$$

ρ(z), $u_\upsilon(r)$ and $f_\upsilon(r)$ are molar densities of substance, energy and free energy in transition layer. For spherical nanoparticle in dispersion medium (vapor) we get

$$\bar{u} = \left(u_\upsilon^{(\beta)} - u_\upsilon^{(\alpha)}\right) \Delta r_{eu} \left[1 - \frac{\Delta r_{eu}}{r_e} + \frac{1}{3} \left(\frac{\Delta r_{eu}}{r_e} \right)^2 \right], \qquad (9)$$

$$\sigma = \left(f_{\upsilon}^{(\beta)} - f_{\upsilon}^{(\alpha)}\right)\Delta r_{eu}\left[1 - \frac{\Delta r_{eF}}{r_e} + \frac{1}{3}\left(\frac{\Delta r_{eF}}{r_e}\right)^2\right], \qquad (10)$$

where $\Delta r_{eu} = r_e - r_u$ and $\Delta r_{eF} = r_e - r_F$ – distances from the equimolar dividing surface to the separating surfaces corresponding to the conditions of $\overline{u} = 0$ and $\overline{F} = 0$. Switching to the planar case ($r_e \to \infty$) and after some transformations we obtain

$$\overline{u}_{\infty} = \frac{\Delta H - RT}{\upsilon}\Delta z_{\overline{u}}, \qquad (11)$$

$$\sigma_{\infty} = \mu\left(\rho^{(\beta)} - \rho^{(\alpha)}\right)\Delta z_{\sigma}, \qquad (12)$$

where $\Delta z_{\overline{u}} = \lim_{r_{eu}\to\infty}\Delta r_{eu}$, $\Delta z_{\sigma} = \lim_{r_{eu}\to\infty}\Delta r_{eF}$, ΔH – the heat of phase transition $\alpha \to \beta$, μ – chemical potential in the bulk ($\mu = \mu^{(\alpha)} = \mu^{(\beta)}$).

The equations (9) and (10) are taken from [1], while (10) and (12) – from [2]. If Δr_{eu} and Δr_{eF} are supposed to be independent from the radius r_e (as Tolman accepted in his formula for $\sigma(r)$ [3]), then it comes from (9)-(12) that

$$\overline{u}(r) = \overline{u}_{\infty}\left[1 - \frac{\Delta z_{\overline{u}}}{r_e} + \frac{1}{3}\left(\frac{\Delta z_{\overline{u}}}{r_e}\right)^2\right], \qquad (13)$$

$$\sigma(r) = \sigma_{\infty}\left[1 - \frac{\Delta z_{\sigma}}{r_e} + \frac{1}{3}\left(\frac{\Delta z_{\sigma}}{r_e}\right)^2\right], \qquad (14)$$

where $\Delta z_{\overline{u}} = \Delta z_{eu}$, $\Delta z_{\sigma} = \Delta z_{eF}$.

Using (11) and (12) one can, if knows the values of $\overline{u}_{\infty}$ and σ_{∞}, calculate $\Delta z_{\overline{u}}$ and Δz_{σ} and then find dependences for $\overline{u}(r)$ and $\sigma(r)$ according equations (13) and (14). Similar calculations of $\Delta z_{\overline{u}}$ on the basis of experimental data on $\overline{u}_{\infty}$ (obtained from Gibbs-Helmholtz formula and on measured values of σ and $d\sigma/dT$) were performed for 20 metals in [1].

Here we present calculation for 50 liquid metals, results for $\Delta z_{\overline{u}}^{(E)}$ being collected in Table 1. The values of $\Delta z_{\overline{u}}^{(E)}$ for the same 50 liquid metals obtained on the basis of experimental data of σ are reported in [2] by us.

Now we are going to define the relations for the $\Delta z_{\overline{u}}$ and Δz_{σ}. Following [2] we have

$$\Delta z_{\sigma} = B_{\sigma}\upsilon^{1/3}, \qquad (15)$$

where υ – molar volume of the liquid and the constant B_{σ} is $0{,}128\cdot10^{-8}$, $0{,}140\cdot10^{-8}$ and $0{,}204\cdot10^{-8}$ for bcc, fcc and hcp – structures of premelting respectively, $B_{\sigma} = 0{,}284\cdot10^{-8}$ for liquid Hg possessing rombohedron structure of premelting.

The value of $\Delta z_{\overline{u}}$ will be found self-consistently availing isotropic model for the liquid metal [4] and using Gibbs-Helmholtz formula $\overline{u}_{\infty} = \sigma_{\infty}\left(1 - \frac{T}{\sigma_{\infty}}\frac{d\sigma_{\infty}}{dT}\right)$. The term in round brackets of the latter can be approximately estimated, following [3], as

$$1 - \frac{T}{\sigma_{\infty}}\frac{d\sigma_{\infty}}{dT} \simeq \frac{L_0}{L_0 - 3RT\ln 2} - \frac{2}{3}\frac{T}{D}\frac{dD}{dT}, \qquad (16)$$

where L_0 – heat of evaporation of the overcooled liquid at absolute zero temperature (per mole), D – density (of mass) of liquid metal, dD/dT – temperature coefficient of the density, R – universal gas constant. Now, using (11) and (12) we have

$$\Delta z_{\overline{u}} = B_{\overline{u}}\upsilon^{1/3}, \qquad (17)$$

where

$$B_{\overline{u}} = B_{\sigma}\frac{\mu}{RT - \Delta H}\left(\frac{L_0}{L_0 - 3RT\ln 2} - \frac{2}{3}\frac{T}{D}\frac{dD}{dT}\right). \qquad (18)$$

The values of ΔH, D, dD/dT, L_0 and B_{σ} entering (18) are known, the chemical potential can be found as $\mu = RT\ln\lambda = RT\ln[V_Q \cdot P/(kT)]$, where λ – activity, P – vapor pressure, $V_Q = [2\pi\hbar^2/(a_0 AkT)]^{3/2}$ – quantum volume, A – atomic mass, $\hbar = h/2\pi$, k – Boltzmann constant, $a_0 = 1{,}6604\cdot10^{-24}$ grams.

We have calculated parameters of $\Delta z_{\overline{u}}$ and Δz_{σ}, values of surface energy $\overline{u}_{\infty}$ and surface tension σ_{∞} and size dependences of $\overline{u}(r_e)$ and $\sigma(r_e)$ at melting point with the above equations for the 50 liquid metals. The bulk properties of liquid metals needed for the calculus were taken from [2]. The required quantities of ΔH, dD/dT and $d\sigma/dT$ for liquid metals (absent in [2]) are given in Table 1. The values of L_0 were calculated on the known ΔH according [4]. The full data for the calculation of values related to the surface tension (Δz_{σ}, σ_{∞} and $\sigma(r)$) are presented in [2] for all metals.

The results of calculations demonstrate (Table 1) that the size parameters $\Delta z_{\overline{u}}$ and Δz_{σ} are positive in sign for all metals and negligible in absolute measure (they are less than average distance between particles in the liquid). The former reveals that the equimolar surface is farther than rest mentioned dividing surfaces corresponding to the zero excess free energy ($\overline{F} = 0$) and zero cohesion energy ($\overline{u} = 0$). The trifle values of Δz_{σ} and $\Delta z_{\overline{u}}$ confirm the relevant proximity of the profiles of density and free energy as well as of density and potential energy in surface layer. Besides, the dividing surface corresponding to zero cohesion energy is closer to the condensed phase in comparison to the dividing surface determined by zero excess free energy in the transition layer, the physical boundary liquid-vapor being the same at melting point.

Table 1. The values of $\Delta z_{\bar{u}}$, Δz_{σ}, surface energy $\bar{u}_{\infty}$ and surface tension σ_{∞} for the flat boundary liquid metal – vapor at melting point (the given are also input data on ΔH, υ, dD/dT, $d\sigma/dT$)

Metal / premelting structure	ΔH, $J/mole$	υ $10^{-6}, m^3$	$-\frac{d\rho}{dT}$ $\frac{kg}{m^3 \cdot K}$	$-\frac{d\sigma}{dT}$, $\frac{mJ}{m^2 \cdot K}$	$\Delta z_{\bar{u}}^{(E)}$, $10^{-10} m$	$\Delta z_{\bar{u}}^{(T)}$, $10^{-10} m$	$\frac{\Delta z_{\bar{u}}^{(E)}}{\Delta z_{\sigma}^{(E)}}$	$\bar{u}_{\infty}^{(E)}$, $\frac{mJ}{m^2}$	$\bar{u}_{\infty}^{(T)}$, $\frac{mJ}{m^2}$	$\frac{\bar{u}_{\infty}}{\sigma_{\infty}}$	$\frac{\bar{u}^{(E)} - \bar{u}^{(T)}}{\bar{u}^{(E)}} \times 100\%$
Li bcc	134686	13,221	0,052	0,150	0,475	0,421	1,386	463,1	410,98	1,104	11,25
Na bcc	9037,66	24,277	0,236	0,090	0,642	0,578	1,563	227,39	204,79	1,107	9,94
K bcc	79000	47,683	0,229	0,070	0,786	0,717	1,545	125,59	114,58	1,134	8,77
Rb bcc	76000	58,135	0,486	0,053	0,904	0,836	1,679	103,54	95,8	1,127	7,47
Cs bcc	65899,58	72,228	0,638	0,045	0,942	0,926	1,734	82,64	81,26	1,145	1,66
Be bcc	294560	6,346	0,116	0,156	0,361	0,360	1,513	1603	1598	1,175	0,34
Mg hcp	127405,86	15,286	0,265	0,150	0,928	0,967	1,751	727	757,14	1,231	-4,20
Ca bcc	183920	27,640	0,221	0,062	0,629	0,642	1,662	398	405,20	1,224	-1,92
Sr fcc	144000	35,331	0,262	0,060	0,908	0,941	2,045	348	360,32	1,205	-3,68
Ba bcc	150920,51	41,352	0,526	0,07	1,002	0,996	2,254	346	343,86	1,219	0,56
Cu fcc	304364	7,905	0,801	0,21	0,441	0,439	1,508	1635	1628	1,163	0,43
Ag fcc	255062	11,519	0,907	0,125	0,506	0,519	1,643	1074	1103	1,161	-2,68
Au fcc	330962,34	11,591	1,500	0,190	0,516	0,509	1,610	1424	1403	1,147	1,46
Zn hcp	114657	9,923	1,100	0,260	0,883	0,821	1,717	969,18	900,69	1,185	7,07
Cd hcp	99874,48	14,023	1,160	0,080	0,897	0,901	1,681	607,54	610	1,162	-0,40
Al fcc	290794,98	11,384	0,280	0,146	0,429	0,437	1,382	1066	1086	1,131	-1,81
Ga bcc	249372,39	11,482	0,662	0,088	0,356	0,369	1,168	764,66	793,60	1,041	-3,79
In bcc	219665	16,126	0,430	0,081	0,433	0,401	1,238	579,81	537,60	0,922	7,29
Tl bcc	173430,96	18,071	1,430	0,080	0,561	0,489	1,455	497,1	433,58	1,106	12,77
Tl fcc					0,561	0,536	1,455	497,1	474,9	1,107	4,47
Fe bcc	341464,43	7,757	0,883	0,230	0,540	0,457	1,799	2273	1923	1,240	15,39
Fe fcc					0,540	0,530	1,799	2273	2104	1,240	7,40
Co fcc	355941,42	7,312	0,988	0,340	0,533	0,480	1,746	2431	2186	1,733	10,08
Ni fcc	353514,64	7,424	1,160	0,330	0,518	0,485	1,769	2340	2191	1,269	6,39
Rh fcc	495000	9,528	0,896	0,300	0,517	0,484	1,624	2586	2420	1,222	6,43
Ir fcc	558410,04	9,913	0,935	0,230	0,532	0,487	1,668	2876	2632	1,101	8,46
Pt fcc	468619,25	10,423	2,900	0,310	0,576	0,561	1,871	2494	2433	1,282	2,46
Ti bcc	470711,30	11,678	0,702	0,200	0,457	0,444	1,530	1778	1727	1,293	2,88
Zr bcc	581590	15,728	0,310	0,17	0,516	0,488	1,517	1732	1638	1,142	5,41
Hf bcc	661087,87	16,080	2,318	0,210	0,567	0,611	1,946	2113	2277	1,291	-7,75
V bcc	458577,41	7,383	0,531	0,230	0,403	0,393	1,571	2404	2343	1,193	2,55
Nb bcc	609623,4	11,865	0,800	0,170	0,482	0,420	1,411	2305,8	2007,3	1,026	12,95
Ta bcc	770292,89	12,063	1,147	0,250	0,523	0,485	1,650	3222	2987	1,243	7,28
Cr bcc	392050,21	8,112	0,300	0,200	0,521	0,480	1,847	1973	1816,8	1,207	7,90
Mo bcc	630233,47	10,272	0,743	0,180	0,449	0,450	1,617	2651	2653	1,228	-0,10
W bcc	823849,37	11,349	1,250	0,210	0,459	0,475	1,680	3297	3415	1,226	-3,58
Mn fcc	243514,64	9,066	0,700	0,200	0,646	0,578	1,928	1393	1246	1,228	10,59
Re bcc	732217,57	9,852	0,800	0,180	0,477	0,461	1,671	3403	3294	1,133	3,20
Sn bcc	230125,52	17,179	0,194	0,160	0,509	0,494	1,496	670	649	1,049	3,04
Pb fcc	177824,27	19,097	1,317	0,085	0,559	0,552	1,477	506	500	1,104	1,20
Bi bcc	170962,34	20,938	1,200	0,0766	0,524	0,491	1,394	417	390	1,099	6,42
Hg rhomb	59297,07	14,749	2,400	0,281	1,447	1,456	1,394	563	566	1,095	-0,58
Ru fcc	527447,7	9,272	2,146	0,310	0,555	0,611	2,078	3032	3337	1,413	-10,04
Tb bcc	356900	21,950	0,152	0,060	0,510	0,563	1,572	797,8	880,7	1,104	-10,38
Os bcc	748954	9,463	3,655	0,330	0,471	0,483	1,949	3589	3685	1,354	-2,67
Ce bcc	350000	20,96	0,227	0,070	0,541	0,520	1,469	880	846	1,078	3,84
Pr bcc	296652,7	21,314	0,240	0,080	0,597	0,547	1,544	802,4	735,25	1,101	8,37
Nd bcc	317782	21,567	0,528	0,065	0,541	0,545	1,531	771	776	1,137	-0,71
Gd bcc	305000	22,024	0,793	0,060	0,698	0,738	2,062	925	978	1,208	-5,74
Th bcc	514000	22,099	1,847	0,140	0,618	0,641	1,919	1391	1442	1,207	-3,63
U bcc	420000	13,298	1,031	0,140	0,537	0,500	1,634	1650	1534	1,111	7,04
La bcc	382845	23,326	0,237	0,110	0,548	0,515	1,407	876	823,5	1,088	6,03

Calculations show that $\Delta z_{\bar{u}} > \Delta z_{\sigma}$ all the time what tells that the size effects of surface energy start emerging for bigger particles compared to the surface tension.

The results show that $\Delta z_{\bar{u}}$, and also Δz_{σ}, change "in-shape" with the molar volume and become larger with increasing temperature.

The latter can be associated, as mentioned in [1], to the increasing diffusion and thickness of the transition layer when heating liquid metal. It comes from Table 1 that calculated values of surface energy $\overline{u}_{\infty}^{(T)}$ and surface tension $\sigma_{\infty}^{(T)}$ of liquid metals appearing on flat boundary surrounded by saturated vapor at melting point agree well with the most reliable experimental data for all 50 elements. The values of $\overline{u}_{\infty}^{(E)}$ were calculated on the measured data of $\sigma_{\infty}^{(E)}$ and $d\sigma^{(E)}/dT$. The parameters of $\Delta z_{\overline{u}}$, obtained by theory, $\Delta z_{\overline{u}}^{(T)}$, and by experiment, $\Delta z_{\overline{u}}^{(E)}$, agree quite well too.

The calculations of size dependence $\overline{u}(r)$ and $\sigma(r)$ were carried out in range from $r_{e\min} = \Delta z_{\overline{u}}$ and $r_{e\min} = \Delta z_{\sigma}$ to $r_e = \infty$ respectively. One can easily see that the relations $\overline{u}(r_{e\min}) = \overline{u}_{\infty}/3$ and $\sigma(r_{e\min}) = \sigma_{\infty}/3$ are valid at given minimal radii $r_{e\min}$. The calculations for the smaller sizes are out of matter due to the negligibility of $\Delta z_{\overline{u}}$ and Δz_{σ}, see Table 1 (they are less than 10 nanometers except for the mercury), and, the more, there is no reason to ignore the dependence of $\Delta z_{\overline{u}}$ and Δz_{σ} on radius (as assumed afore) in case of extremely curved boundaries.

Calculations show that $\overline{u}(r_e)$ and $\sigma(r_e)$ monotonically decrease with decreasing radius of the particle ($d\overline{u}/dr_e > 0$, $d\sigma/dr_e > 0$) in mentioned ranges of sizes. The same comes from the calculated data of Table 2 for some liquid metals. The similar data for the surface tension of some other liquid metals were published in [2].

So, equations obtained here allow one to calculate the surface energy $\overline{u}$ and the surface tension σ of liquid metals on flat as well as curved surfaces within the unitary approach. The final equations for $\overline{u}$ and σ involve parameters $B_{\overline{u}}$ and B_{σ} dependent on type of premelting structure being either bcc, fcc or hcp.

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Table 2. The size dependence of the surface energy $\overline{u}(r_e)$ and of surface tension $\sigma(r_e)$ of liquid metals at melting point

r_e, nm	$\overline{u}(r_e)$, mJ/m^2					$\sigma(r_e)$, mL/m^2				
	K	Rb	Au	Pt	Mo	K	Rb	Au	Pt	Mo
0,1	52,74	38,14	815,60	1333,27	1638,85	61,57	50.06	852,23	1366,75	1599,68
0,5	106,88	85,95	1282,10	2217,72	2420,07	92,71	78.40	1100,75	1752,78	2015,41
1	115,98	94,46	1351,79	2353,10	2533,75	97,28	82.62	1135,02	1805,85	2072,17
2	120,72	98,93	1387,58	2422,86	2591,93	99,62	84.79	1152,42	1832,79	2100,95
3	122,34	100,45	1399,65	2446,42	2611,52	100,41	85.52	1158,26	1841,83	2110,61
4	123,14	101,22	1405,71	2458,26	2621,35	100,81	85.89	1161,19	1846,36	2115,44
5	123,63	101,68	1409,35	2465,38	2627,27	101,04	86.11	1162,95	1849,08	2118,35
10	124,61	102,61	1416,66	2479,66	2639,11	101,52	86.56	1166,47	1854,54	2124,17
20	125,10	103,07	1420,33	2486,82	2645,05	101,76	86.78	1168,23	1857,27	2127,08
30	125,26	103,23	1421,55	2489,21	2647,03	101,84	86.85	1168,82	1858,18	2128,06
40	125,34	103,31	1422,16	2490,41	2648,03	101,88	86.89	1169,12	1858,63	2128,54
50	125,39	103,35	1422,53	2491,13	2648,62	101,90	86.91	1169,29	1858,91	2128,83
100	125,49	103,45	1423,27	2492,56	2649,81	101,95	86.96	1169,65	1859,45	2129,42
200	125,54	103,49	1423,63	2493,28	2650,40	101,98	86.98	1169,82	1859,73	2129,71
∞	125,59	103,54	1424,00	2494,00	2651,00	102,00	87,00	1170,00	1860,00	2130,00

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