Investigation of size dependences of surface tension and evaporation heat of aluminum droplets using different pair potentials

N.Yu. Sdobnyakov, V.M. Samsonov, A.N. Bazulev,
D.A. Kulpin, D.N. Sokolov

Tver State University, 35 Sadovyi per., 170100 Tver, Russia

The surface tension and the evaporation heat of aluminum nanodroplets are calculated on the basis of the thermodynamic perturbation theory. The size dependences of the surface tension and of the evaporation heat obtained using Schommers potential were compared with the results corresponding to other effective pair potentials. It has been found that Schommers potential provides a better agreement between calculated asymptotical values of the surface tension and the evaporation heat with the available experimental data.

На основе термодинамической теории возмущений проведены расчеты поверхностного натяжения и теплоты испарения для нанокапель алюминия. Размерные зависимости для поверхностного натяжения и теплоты испарения, полученные с использованием потенциала Шоммерса, сопоставлены с результатами, отвечающими другим эффективным парным потенциалам. Установлено, что асимптотические значения поверхностного натяжения и теплоты испарения, отвечающие большим размерам нанокапель и полученные с использованием потенциала Шоммерса, лучше согласуются с имеющимися экспериментальными данными.

1. Introduction

There is an opinion that correct calculation of some properties of metals is not possible using effective pair potentials. Respectively, in these cases many body potentials should be used. For example, any pair potential will inevitably give noticeable mistakes in values of some elastic constants for metals and wrong correlation between the energy of the defect (vacancy) formation and the cohesion energy [1]. At the same time, there is another opinion [2] that the pair interaction model is adequate, to a greater or less extent, for any simple substances including metals which have close packed structure in their solid state. According to [2], the main advantage of many body potentials is that they make it possible to describe properties of systems with lower density, e.g. semiconductors (germanium and silicon). So, the problem of using of pair and many body potentials for metals

have not been solved in a proper way. Some many body potentials are rather sophisticated. So, the cases when properly chosen pair potentials make is possible to predict thermodynamic and some other characteristics of bulk metal phases and their surfaces exactly enough are of special interest. The Schommers potential [3] for aluminum can be treated as an example of modern pair potentials for metals. This potential was developed combining the theory of the pseudopotential with a phenomenological approach and the concept of the effective pair potential.

The purpose of Schommers investigations was to increase the accuracy of calculations and to extend the applicability of effective pair potentials to metal surfaces and nanostructures. Due to additional adjustment of free parameters of Schommers potential for various experimental data (the melting temperature, the diffusion coefficient in the liquid phase, the structure of solid and liq-

uid phases, the photon density, the mean square fluctuation on surfaces etc.) this potential describes all basic properties of aluminum in a wide temperature range [3,4].

One of main goals of this paper is the approbation of Schommers potential on the calculation of the excess free energy of aluminum nanodroplets using a version of the thermodynamic perturbation theory (TPT) proposed in 1960s by L.M.Shcherbakov [5] (see also [6]).

2. Calculation procedure

Besides, the heat of evaporation and its size dependence were analyzed as this quantity is closely interrelated with the size dependence of the specific excess free energy. According to the version of TPT mentioned above, the excess free energy of a small object Ψ is equal to the half of the perturbation energy necessary to cut out the volume V_1 corresponding to the unperturbed droplet from the bulk liquid. In other words, the droplet consisting of N_1 atoms is compared with the volume V_1 in the corresponding bulk phase containing N_1 atoms. According to TPT [7], the perturbation energy 2Ψ should be calculated using the unperturbed Gibbs distribution and, respectively, the unperturbed binary correlation function is equal to the radial distribution function $g_0(r)$. So,

$$\Psi = -\frac{1}{2}(n_l - n_g)^2 \int_{V_1} dV_1 \int_{V_2} dV_2 g_0(r)\Phi(r), \quad (1)$$

where $\Phi(r)$ is the pair potential, r is the intermolecular distance, V_2 is the volume adjacent to the sphere of volume V_1 chosen in the bulk liquid phase, n_l and n_g are densities of atoms in liquid and vapor phases, correspondingly. As we have chosen the equimolecular dividing surface (R), the specific excess free energy

$$\sigma(R) = \Psi / 4\pi R^2 \quad (1')$$

will be equal to the surface tension, which, in turn, is defined as the work of the small object formation per unit area of the dividing surface.

One of the advantages of the TPT variant in question is that it can be applied both to molecular systems and metal particles. In fact, effective pair potentials for metal melts were obtained for bulk phase, and for this case they take into account contributions of electron-ion, ion-ion and electron-electron interactions adequately

enough. So, direct applying of these potentials to very small objects is not quite correct. However, algorithm based on TPT presupposes that the perturbation energy is calculated using the nonperturbed distribution function (i.e. the radial distribution function). As the radial distribution function (RDF) depends on the pair potential, the condition of nonperturbancy of RDF gives also the condition of nonperturbancy of the pair potential, i.e. the potential for the bulk melt phase should be used. So, calculation of the excess free energy Ψ reduces to calculation of 6-dimentional integral figuring in the right-hand side of (1). This calculation was carried out using Monte Carlo method.

The size dependence of the evaporation heat $\lambda(R)$ was investigated in [8] using the surface enthalpy H_S introduced by Guggenheim [9]. The droplet evaporating enthalpy can be written as follows

$$\Delta H = H'' - (H' + H_S), \quad (2)$$

where H' and H'' are the enthalpies of the bulk vapor and liquid phases, respectively. According to [8] the specific evaporation heat λ can be written as

$$\lambda = h'' - h' - \partial H_S / \partial m, \quad (3)$$

where h'' and h' are corresponding specific enthalpies of bulk phases. Equation (3) can be considered as a definition of the specific evaporation heat for a small droplet. This definition gives the expression

$$\Delta\lambda = -v'_\infty \left[\frac{2w}{R} + \frac{\partial w}{\partial R} \right] \quad (4)$$

for $\Delta\lambda = \lambda(R) - \lambda_\infty$, where $\lambda_\infty = h'' - h'$ is the specific evaporation heat for bulk phase, $v'_\infty = 1/\rho_\infty$ is the specific volume of liquid (ρ_∞ is the density of liquid), w is the specific total surface energy (using the Gibbs-Helmholtz equation $\sigma = w + T\frac{d\sigma}{dT}$). In [10] another definition of the evaporation heat $\lambda_0(R)$ was proposed for a small droplet of radius R and mass m_0:

$$\lambda_0 = h'' - h' - H_S / m_0, \quad (3')$$

Then, instead of (3), we will have

$$\Delta\lambda_0 = \lambda_0 - \lambda_\infty = -v'_\infty \frac{3w(r)}{R} + v'_\infty \left(\frac{\sigma}{R} - \frac{\partial\sigma}{\partial R} \right). \quad (4')$$

A conclusion can be made that both (3) and (3') are correct but correspond to the different definitions of the specific evaporation heat. In fact, λ should be interpreted as the quantity of heat necessary to reduce the droplet mass by dm. In turn, λ_0 is the mean value of λ, i.e. it is equal to the specific heat corresponding to the complete evaporation of the droplet. So,

$$\lambda_0 = \overline{\lambda} = \tag{5}$$

$$= m_0^{-1} \int_0^{m_0} \frac{\partial H}{\partial m} dm = h'' - h' - m_0^{-1} \int_0^{m_0} \frac{\partial H_S}{\partial m} dm.$$

Taking into account that the last term in the right-hand side of (5) corresponds to a small correction to the macroscopic value $\lambda_\infty = h'' - h'$, we can conclude that the difference between $\lambda(R)$ and $\lambda_0(R)$ is very small.

3.Results and discussion

We have made comparative calculations of the size dependence of the specific excess free energy for aluminum nanodroplets at 1000 K using Schommers' [3], Morse's [4] and Schiff's [11] potentials. The first of them is presented in [3] numerically. The two others can be written as follows:

$$\Phi_{Morse}(r)= \tag{6}$$
$$= \varepsilon \left\{ \exp[2\alpha(r - r_m)] - 2\exp[\alpha(r - r_m)] \right\},$$

$$\Phi_{schiff}(r) = \tag{7}$$
$$= \varepsilon \{ [cos(8.97r/r^3](0.66 + 4.22/r^2 - 2.61/r^4) +$$
$$+ [sin(8.97r)/r^4](-0.54 = 0.67/r^2) + 1.49/r^{12} \}.$$

where α is a Morse's constant, r_m is the distance corresponding to the minimum of the potentials.

It is of interest to compare Schommer' potential with Morse's one for which the potential well depth ε_c is defined from the melting temperature T_m ($\varepsilon_c = kT_m$) and using another Morse's curve fitted to Schommers potential. Contrary to Morse's potential Schommers one has large oscillations caused by ion-electron interaction in metal crystals. The choice of the temperature ($T = 1000$ K) for comparison of the above potentials and other calculations is dictated by the data on Schommers potential which are given in [3] just for this temperature. The values of parameters figuring in
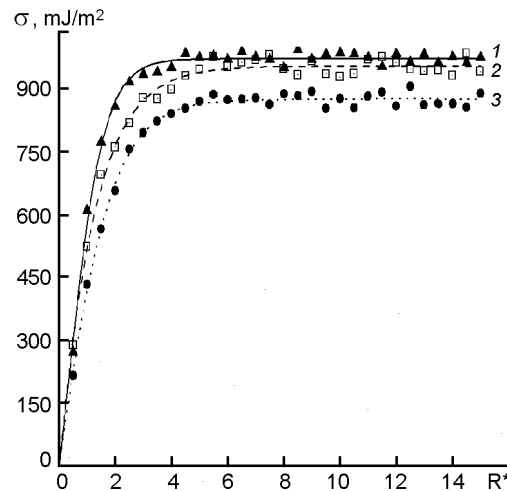

Fig. 1. Dependences of the specific excess free energy for aluminum nanodroplets on the reduced droplet radius $R^* = R/a$ obtained using different pair potential using formula (1') at $T = 1000$ K (curve *1* (approximation data curve) corresponds to Morse's potential with revised value of the potential well depth, curve *2* (approximation data curve) have been calculated for Morse's potential fitted to Schommers potential, curve *3* (approximation data curve) have been found for Schommers potential). Parameters of all the above potentials are given in Table 1.

Table 1. Parameters of used effective pair potentials for Al nanodroplets. Here and later index 1 corresponds to the case when Morse's potential parameters fitted to Schommers potential and index 2 – Morse's potential parameters fitted to Schommers potential for which the potential well depth value have been revised according to the melting temperature. Here a is the effective diameter of aluminum.

Potential	ε, 10^{-21} J	a, Å	α, Å^{-1}	r_m, Å
Schommers	14,09	2,48	–	–
Morse[1]	14,50	2,48	2,50	2,75
Morse[2]	12,88	2,55	1,03	3,23
Schiff	16,53	2,56	–	–

the above interatomic potentials were taken from [3, 4, 11] with no additional fitting using experimental macroscopic values of the surface tension and the heat of evaporation. The parameters in question are presented in Table 1.

In this paper RDF corresponding to different pair potential was calculated using the following equation

$$g(r)/g_{LD}(r) = \exp[-(\Phi(r) - \Phi_{LD}(r))/kT], \quad (8)$$

where $g_{LD}(r)$ is the radial distribution function of the Lennard-Jones fluid. The last one was calculated according to Matteoli and Mansoori [12].

The obtained values of the surface tension for aluminum were compared with Tolmen's formula [13]

$$\sigma/\sigma_\infty = (1 + 2\delta/R_s)^{-1}, \quad (9)$$

where R_s is the radius of the surface of tension (below the index s will be omitted), $\delta > 0$ is the distance between the equimolecular separating surface and the surface of tension for a flat interface. Thus, the parameter δ, the so-called Tolmen's length, should be comparable with the effective molecular diameter a. For small R, A.I. Rusanov [14] obtained a linear dependence

$$\sigma = KR. \quad (10)$$

Here K is the proportionality coefficient depending on the temperature, the pressure and the liquid phase composition. Results of calculations for the specific excess free energy show that the form of the dependences does not depend on the choice of the intermolecular interaction potential. Then, in a satisfactory approximation, the following formula can be used

$$\sigma(R) = \begin{cases} KR, & \text{if } R \leq R_c \\ \sigma_\infty, & \text{if } R > R_c \end{cases}, \quad (11)$$

i.e. for $R < R_c$ (R_c is a characteristic radius) the surface tension is described by Rusanov's linear formula, and, for $R > R_c$, it is nearly equal to the maximum value σ_∞ of $\sigma(R)$, corresponding to the flat macroscopic surface. Table 2 demonstrates the calculation results for the macroscopic surface tension σ_∞. The Tolmen's parameter δ and the coefficient K for aluminum nanodroplets at 1000 K have been obtained using different pair potentials. One can see that calculation results corresponding to Schommers potential agree with experimental data [15-17] more satisfactorily.

Fig. 2 demonstrates the size dependence of the evaporation heat for aluminum nanodroplets obtained using Schiff's and Schommers potentials. One can see that the size
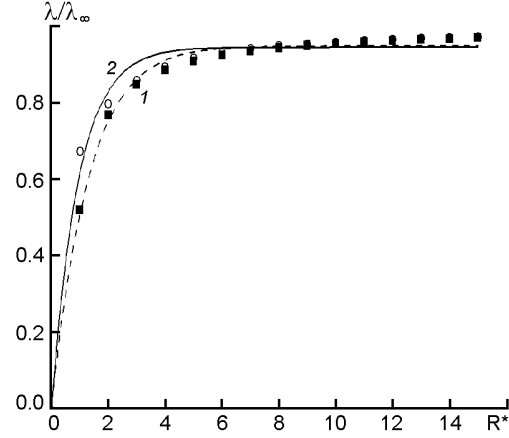

Fig. 2. Dependences of the evaporation heat for aluminum on the reduced droplet radius $R^* = R/a$ obtained for different effective pair potentials using formula (4') at $T = 1000$ K (curve *1* (approximation data curve) corresponds to Schiff's potential, curve *2* (approximation data curve) was obtained using Schommers potential). Parameters of potentials are presented in Table 1.

dependence of the specific evaporation heat $\lambda(R)$ can be described, in a good approximation, by a formula analogous to Eq. (11). In other words, if $R \leq R_c$ evaporation heat $\lambda(R)$ linearly decreases when the particle size decreases, and if $R > R_c$ $\lambda(R)$ is nearly equal to the maximum value λ_∞ corresponding to $R \to \infty$ i.e. to the macroscopic liquid phase.

The linear approximation for the evaporation heat of nanoparticles at $R \to 0$ gives the next relationship

$$\lambda_\infty = 3K_w\nu'_\infty, \quad (12)$$

where $K_w = K_w(p, T)$ is proportionality coefficient for the specific total surface energy. This coefficient is analogous to the proportionality coefficient in (11).

The macroscopic value of specific evaporation heat can be calculated using the following formula [10]

$$\lambda_\infty = (n_g/n_l - 1)u_1 + kT, \quad (13)$$

where $u_1 = 2\pi n_l \int_0^\infty g_0(r)\Phi(r)r^2 dr$ is the internal energy of liquid per an atom. We have calculated the molar evaporation heat values for aluminum using different potentials

Table 2. Calculation results for σ_∞, δ and K corresponding to Al nanodroplets. The experimental values of the surface tension at the 1000 K are 885 mJ/m^2 [15], 856 mJ/m^2 [16] and 891 mJ/m^2 [17].

Potential	σ_∞, Å^{-1}	K, 10^{10} mJ/m^3	δ, Å^{-1}
Schommers	874	88	0.69
Morse[1]	953	96	0.60
Morse[2]	972	95	0.51
Schiff	964	94	0.40

Table 3. Calculated macroscopic values of the heat of evaporation for Al nanodroplets. The experimental values of the evaporation heat at the 2793 K is 293 kJ·mol^{-1} [15].

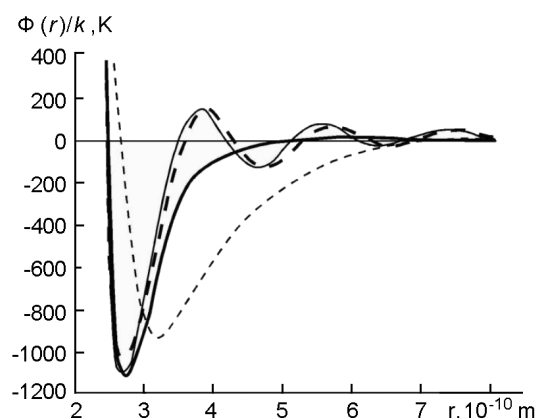| Potential	λ_∞, mJ·mol^{-1}	Potential	λ_∞, mJ·mol^{-1}
Schommers	338	Morse[1]	297
Schiff	310	Morse[2]	323

Fig. 3. Comparison of the Schommers and Morse pair potentials for aluminium. The Schommers potential was built at temperatures of 300 K (the dark solid curve) and 1000 K (the light dashed curve). The Morse potential adjusted to the Schommers potential (the light solid curve), the Morse potential with the depth have been revised according to the melting temperature (the dark dashed curve). The melting temperature of aluminium is 993 K, k is the Boltzmann constant.

(see Table 3). A difference between calculated and experimental [15] values can be caused by the difference in temperatures (we could not find experimental data on λ_∞ for $T = 1000$ K). One can see that the results for the evaporation heat calculated using different potentials agree with experimental data. One can note that calculated values of σ_∞ and λ_∞ for aluminum obtained using Morse's effective pair potential (6) with no large-scale oscillations, Schommers potential and Schiff's potential (7), show a satisfactory agreement. Size dependences (Fig. 2) also demonstrate agreement with experimental values λ_∞.

4. Conclusion

We must emphasize that the choice of the definite temperature for comparison of the above potentials was dictated by the available data on Schommers potential which are given in [3] just for this temperature. However the method of the thermodynamic perturbation theory was applied for investigation surface tension of the metal nanodroplets for the different pair potentials in our previous works [18−20] in a wide temperature range from the melting point to the critical temperature. In addition to the problem of curvature corrections to the macroscopic value of the heat of evaporation λ_∞ of liquid metals was investigated on the basis of thermodynamic analysis and Monte Carlo computer simulation of metal nanodroplets [10]. In [10] we conclude that the thermodynamic results are in good agreement with Monte Carlo calculations of the evaporation enthalpy for aluminum nanodroplets.

The Schommers pair potential for aluminium at 1000 K is shown in Fig. 3. It is compared with the respective Morse potential, for which the potential well depth which was found by the melting temperature and with the Morse potential adjusted to the Schommers potential. The difference between the potentials is clear: apart from the different depth and location of the minimum, the Morse potential does not contain any large-scale oscillations determined by ion-electron-ion interaction in metallic crystals (such oscillations has Schiff's potential). For this reason, it is still open to question if one can apply the phenomenological Morse, Lennard-Jones and etc. potentials to describe the interaction in metals. In this work we have shown that effective pair potentials with properly chosen parameters give adequate values of energetic properties of metal nanoparticles as well as of some bulk and surface properties for liquid aluminum. Schommers potential provides a better agreement with the available experiment data on the evaporation

heat and the surface tension of the aluminum melt at least at the temperature $T = 1000$ K. As was mentioned above, Morse's , Schiff's pair potentials can be also applied to describe thermodynamic properties of other liquid metals including for example sodium and copper [20].

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Дослідження розмірних залежностей поверхневого натягу і теплоти випаровування нанокрапель алюмінію з використанням різних потенціалів

М.Ю.Сдобняков, В.М.Самсонов, А.Н.Базулев, Д.О. Кульпін, Д.Н. Соколов

На основі термодинамічної теорії збурень проведено розрахунок поверхневого натягу і теплоти випаровування для нанокрапель алюмінію. Розмірні залежності для поверхневого натягу і теплоти випаровування одержані з викристанням потенціалу Шоммерса, порівняні з результатами, що відповідають іншим ефективним парним потенціалам. Встановлено, що асимптотичні значення поверхневого натягу і теплоти випаровування, що відповідають великим розмірам нанокрапель і одержані з використанням потенціалу Шоммерса, краще узгоджуються з наявними експериментальними даними.